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Enhancement of the Seebeck coefficient in touching M/Bi–Te/M (M = Cu and Ni) composites

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Abstract The resultant Seebeck coefficient α of the touching p- and n-type M/Bi–Te/M (M = Cu and Ni) composites was measured as a function of z at a scan step of 0.5 mm using thermocouples set at three different intervals of $s = 4$, 6.5 and 8 mm, where s is the interval between two probes and z is the distance from the center of Bi–Te compound to the middle of two thermocouples. Bi–Te compounds have a thickness of $t_{\mathrm{Bi–Te}} = 6$ mm but the thickness t_{M} of both end metals sandwiching their compounds was varied from 0.5 mm to 6 mm. The composites were compacted tightly at a force of about 10 N by a ratchet. When two probes are placed on both end metals, the resultant α was significantly enhanced and exhibited a tendency to increase as s approaches $t_{\mathrm{Bi–Te}}$, like the welded composites. The enhancement in α is attributed to the contribution from the barrier thermo-emf generated near the interface. When the thickness t_0 of metal outside two probes set at $s = 6.5$ mm was increased from 0.25 mm to 5.75 mm, the averaged α for M = Cu and Ni was increased by 3.8% in the p-type composite, while reversely it was decreased by 4.8% in the n-type one. It was first observed that t_0 also has a significant influence on the resultant α. The maximum α of the p- and n-type Ni/Bi–Te/Ni composites then reached great values of 264 μV/K at $t_{\mathrm{M}} = 6$ mm (corresponding to $t_0 = 5.75$ mm) and −280 μV/K at $t_{\mathrm{M}} = 1.2$ mm (corresponding to $t_0 = 0.95$ mm), respectively, which are 29% and 23% larger in absolute value than their intrinsic α values. These maximum α were barely changed with time. It was thus found that the barrier thermo-emf is generated steadily even in touching composites and the resultant α is highly sensitive to the position of leads connected to the metal electrode of a thermoelement.

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

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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 of 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 differentiation of this thermo-emf with respect to ΔT, where ΔT is the temperature difference producing the thermo-emf. The appearance of the barrier thermo-emf was indeed observed in 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 the thermoelectric composites [12, 13] corresponding to the metal-semiconductor junction, in which a thermoelectric semiconductor is sandwiched between two metals. For example, the maximum resultant α of the macroscopic p- and n-type Cu/Bi–Te/Cu welded with eutectic solder of Pb–Sn [12] and the n-type M/Bi/M (M = Cu and Ni) welded with Bi [13] was 20–30% higher in absolute value than those of their intrinsic thermoelectric materials. Interestingly, the increase in α of Cu/Bi–Te/Cu composites was not accompanied by the increase in ρ, resulting in the increase in ZT [12]. Such an enhancement in α was observed in welded composites alone, but it has never been observed in touching ones. Of course, the interface structure fitted to increase the degree of enhancement in α has not yet been known. Moreover, it has not yet been investigated whether the barrier thermo-emf generated near the interface of the touching composite is steady in time. 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 resultant α of composites has been dealt as a function of ratio of the thickness t_T of a thermoelectric material to the interval s between two probes [12, 13]. However, the relationship between the thickness t_0 of metal outside two probes and the degree of increase in α of composites has never been discussed. For this reason, the dependence of α on t_0 was also investigated in touching composites.

The purpose of this paper is to investigate whether the resultant α of touching M/Bi–Te/M (M = Cu and Ni) composites is enhanced at a relative thickness of a Bi–Te compound and varies as time passes, and further to study to what degree the volume fraction of metals outside two probes has an influence on α of touching composites.

Calculation and experiments

Calculation of the resultant α of a composite material

Let us consider a composite thermoelectric device (CTD) 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. 1. Here, we derive the resultant α for CTD by treating it as an electrical and thermal circuit [13, 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 the boundary Seebeck coefficient. When the electrical resistivities of the materials M and T are ρ_M and ρ_T, the total electrical resistivity ρ of CTD is expressed as

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

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

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

where $b = \rho_M/\rho_T$. If the thermal conductivities of the

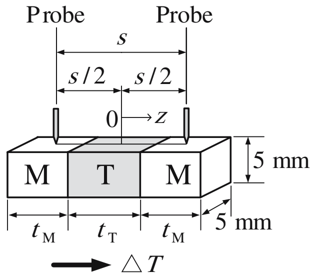

Fig. 1 Touching composite device with a sandwich structure (M/T/M) in which a parallelepiped of thermoelectric material T is touched tightly with two metallic parallelepipeds M at a constant force of 10 N, where s is the interval between two probes, t_T is the thickness (6 mm) of Bi–Te compounds and t_M is the thickness of metals

materials M and T are κ_M and κ_T, the total thermal conductivity κ of CTD is expressed as

$$\kappa = \frac{\kappa_T c}{(1-x)+xc}. \tag{3}$$

where $c = \kappa_M/\kappa_T$. For a given temperature difference ΔT (=($T_H - T_C$)) where T_H and T_C are temperatures of hot and cold sides of CTD, the temperature difference generated in each thermoelectric should be proportional to thickness but inversely proportional to thermal conductivity. Taking this into account, the ratio of ΔT_M to ΔT_T is expressed as

$$\frac{\Delta T_M}{\Delta T_T} = \frac{t_M \kappa_T}{t_T \kappa_M} = \frac{(1-x)}{2cx}. \tag{4}$$

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

$$\Delta T = 2\Delta T_M + \Delta T_T. \tag{5}$$

ΔT_T is derived from Eqs. 4 and 5 as

$$\Delta T_T = \frac{cx\Delta T}{(1-x)+cx}. \tag{6}$$

The total thermal voltage ΔV generated by ΔT_M and ΔT_T is expressed as

$$\Delta V = 2\Delta T_M \alpha_M + \Delta T_T \alpha_T, \tag{7}$$

where α_M and α_T are Seebeck coefficients of the materials M and T. Therefore, the overall Seebeck coefficient α is expressed as

$$\alpha = \frac{\Delta V}{\Delta T} = \frac{\alpha_M(1-x)+\alpha_T cx}{(1-x)+cx} = \frac{\alpha_T\{a(1-x)+cx\}}{(1-x)+cx} \tag{8}$$

using Eqs. 4, 5 and 7, where $a = \alpha_M/\alpha_T$. This equation means that the resultant α is smaller than α_T for any combination of *a, c* and *x*. As pointed out by Balmush et al. [11], however, the resultant α consists of the contribution from both the bulk thermo-emf of the *p*- or *n*-type thermoelectric material and the barrier thermo-emf generated near the interface. Indeed, the resultant α much larger than α_T has been observed in the *p*- and *n*-type Cu/Bi–Te/Cu composites welded with eutectic solder of Pb–Sn [12] and the *n*-type M/Bi/M (M = Cu and Ni) ones welded with Bi [13]. The maximum α appeared at $x = 0.98$ for the former composites and at $x = 0.80$ for the latter ones. The maximum α values of the former *p*- and *n*-type Cu/Bi–Te/Cu were 32% and 30% higher in absolute value than those of the intrinsic *p*- and *n*-type Bi–Te compounds, respectively, and the maximum values of the latter *n*-type M/Bi/M (M = Cu and Ni) were 21% higher in absolute value than that of pure Bi. It is thus certain that the interface between the thermoelectric material and metal contributes to an enhancement in α of composites. As proposed by Dashevsky et al. [15], the resultant α of composites should be derived fundamentally using phenomenological equations for current densities of electrons and holes, the equation of continuity for them, and the Poisson equation for the distribution of electric field perpendicular to the interface. Since the model proposed by them includes many indefinite physical parameters of the interface, however, it is very difficult to estimate precisely the barrier thermo-emf for various cases. Therefore, most of our attention will be directed toward discussing the contribution from the barrier thermo-emf to the total Seebeck coefficient.

Sample-preparation and measurements

The *p*-type $(Bi_{0.25}Sb_{0.75})_2Te_3$ doped with 8 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 [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 ingot 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 [19].

These as-grown *p*- and *n*-type Bi–Te ingots were employed to prepare the touching *p*- and *n*-type M/Bi–Te/M (M = Cu and Ni) composites in which M is compacted tightly with Bi–Te compounds at a constant force of about 10 N using a ratchet, as shown in Fig. 2. The as-grown Bi–Te ingots were cut into a parallelepiped of $5 \times 5 \times 6$ mm^3, where the length of 6 mm is parallel to the freezing direction. Parallelepiped copper and nickel were prepared by cutting a long pillar with a square 5 mm on a side into four different thicknesses of 0.5, 1.2, 2, 4 and 6 mm, where the purity of copper and nickel was 99.99%. Their dimensions are listed in Table 2. Both end surfaces of Bi–Te compounds and

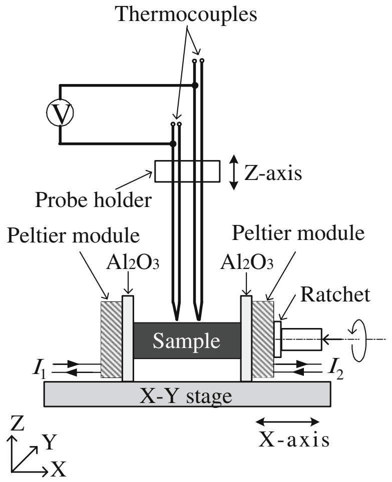

Fig. 2 Schematic configuration for α measurements of composite materials compacted tightly by a ratchet. One end was heated by flowing the electrical current I_1 or I_2 through a Peltier module to produce the temperature differences and another one was then maintained at room temperature. Two alumel–chromel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

metals were polished mechanically by the lapping method to make flat and parallel the touched surfaces. The degree of parallelism of so fabricated specimens was less than 3 μm.

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 $\times$ 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 K to 303 K with the temperature difference of about 10 K. The electrical resistivity ρ was measured concurrently by the four-probe method. 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.

The Seebeck coefficient of the composites compacted tightly by a ratchet was measured using an apparatus fabricated by us. Figure 2 shows a schematic of the apparatus. It has two alumel–chromel thermocouples (0.25 mm in diameter) to detect temperatures and a voltage on the surface of a composite. The composite material is mounted on an X–Y stage and the temperature gradient was applied with two Peltier modules equipped to both ends of the specimen. 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. The resultant α of composites was measured as a function of z at a scan step of 0.5 mm using thermocouples set at three different intervals of s = 4, 6.5 and 8 mm, where s is the interval between two probes and z is the distance from the center of Bi–Te compound to the middle of two thermocouples, as shown in Fig. 1. The measurement of α was made by producing the temperature difference of about 30 K between both ends of Bi–Te compound. 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 accuracy of thermometer to the absolute value of the observed ΔT. The smallest ΔT was approximately 6, 10 and 14 K for probe intervals of s = 4, 6.5 and 8 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 approximately 2.7, 2.0 and 1.7% for probe intervals of s = 4, 6.5 and 8 mm. These errors are denoted by the error bar in Figs. 3–8.

However, the measurement of ρ was not made for the present composites, because the contact resistance is too large to obtain ρ with a high accuracy. It has already been reported by us that when Bi–Te compounds were touched tightly with Cu or Ni, I versus V characteristics of these junctions exhibits an Ohmic behavior [20]. However, their contact resistances were approximately four times as high as the intrinsic resistances of Bi–Te compounds [20].

Results and discussion

Dependence of the resultant α of composites on the probe position

The resultant α of the touching p- and n-type M/Bi–Te/M composites was measured as a function of z, using thermocouples set at an interval of s = 4 mm, in order to compare with those obtained by the conventional method. When $|z| < (t_{\text{Bi–Te}} - s)/2$, two probes are placed on Bi–Te compound, while when $|z| > (t_{\text{Bi–Te}} - s)/2$, one probe is placed on Bi–Te compound and another on metal, where $t_{\text{Bi–Te}}$ is the thickness of Bi–Te compounds. As shown in Fig. 3, the z-dependences of the measured α for the p- and n-type composites exhibit tendencies similar to each other, irrespective to the type of metal. The resultant α has a rather flat hollow in the region of

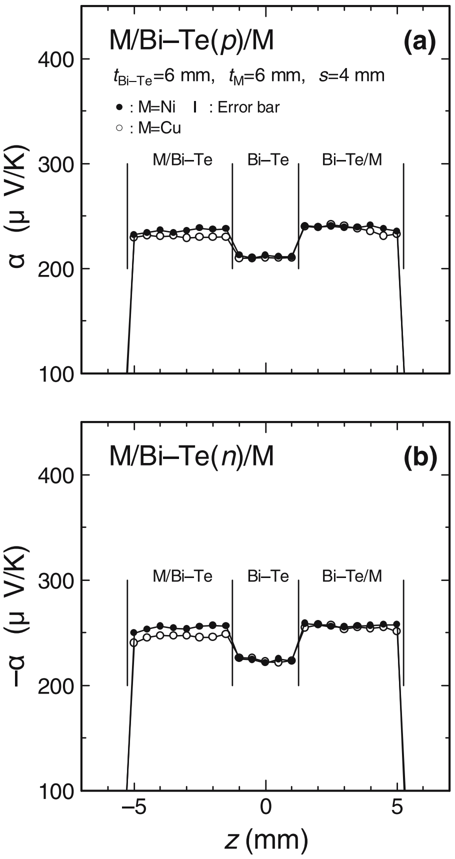

Fig. 3 Resultant α measured as a function of z for the p- and n-type M/Bi–Te/M (M = Cu and Ni) composites, where s = 4 mm and t_M = 6 mm

$|z| < (t_{Bi-Te} - s)/2$, but has greater values in the region of $|z| > (t_{Bi-Te} - s)/2$. The former value indicates the Seebeck coefficient of Bi–Te compounds themselves, and the latter one consists of the sum of the bulk Seebeck coefficient and boundary Sebeck coefficient (caused by the barrier thermo-emf) appeared in the forward-bias direction. The averaged α values of hollows for the p- and n-type composites are approximately +211 and –224 μV/K, respectively, which indeed agree well with those (listed in Table 1) measured at 298 K for the p- and n-type Bi–Te compounds by the conventional technique. The z-dependence of α is almost symmetrical with respect to the origin (z = 0 mm), irrespective of the type of conduction. It indicates that the barrier thermo-emf generated at both Bi–Te/M and M/Bi–Te interfaces points to the same direction, independently of whether M lies in the hot or cold side. In other words, the direction of the polarization of non-equilibrium carriers is the same even at either interface.

Dependence of the resultant α on the thickness of metals

s = 8 mm

The resultant α of the touching p- and n-type M/Bi–Te/M composites was measured as a function of z, using thermocouples set at an interval of s = 8 mm, where the sandwiching metals have four different thicknesses of 1.2, 2, 4 and 6 mm, as listed in Table 2. This combination of t_{Bi-Te} = 6 mm and s = 8 mm corresponds to x = 0.75, which is rather close to x = 0.80, giving the maximum value of α in the n-type M/Bi/M (M = Cu and Ni) composites [13]. As shown in Figs. 4 and 5, the observed α of M/Bi–Te/M has a rather flat plateau in the range from z = –1 to +1 mm and tends to drop abruptly when $|z| > 1$ mm. It indicates that when $|z| < 1$ mm, i.e, two probes are placed on both end metals, α remains almost constant even when z was changed. When t_M was changed, however, α of the p-type M/Bi–Te/M varies significantly with t_M, while that of the n-type one exhibited a little variation with t_M. The averaged α value for a plateau at each t_M was plotted as a function of t_M in Fig. 6, where α at t_M = 0 mm corresponds to the intrinsic Seebeck coefficients listed in Table 1. Interestingly, the resultant α of the p-type composites increases abruptly at t_M = 1.2 mm and tends to increase slowly with further increase of t_M, while that of the n-type ones has a local maximum at t_M = 1.2 mm but tends to decrease slowly with further increase of t_M. In a word, the t_M-dependences of α for the p- and n-type composites exhibit an opposite tendency for $t_M > 1$ mm. This tendency was almost the same, irrespective to the type of metal. It suggests that the barrier thermo-emf itself varies with changes in the length of metal outside two probes. If

Table 1 Thermoelectric properties measured at 298 K for pure Cu and Ni and the p- and n-type Bi–Te compounds

		Cu	Ni	Bismuth–telluride	
				p-type	n-type
Electrical resistivity	ρ (μΩm)	0.0171	0.0720	7.30	10.7
Seebeck coefficient	α (μV/K)	+1.9	– 15	205	– 227
Thermal conductivity	κ (W/mK)	401[a]	91[a]	1.54	1.57
Power factor	P (mW/K^{2}m)	0.21	3.13	5.75	4.82
Figure of merit	ZT	1.57×10^{-4}	1.02×10^{-4}	1.11	0.91
Specific heat	C (J/cm^{3}K)	3.44	3.87	1.22	1.23

[a] Ref. 21

Table 2 Thickness of pure metals (Cu and Ni) and the *p*- and *n*-type Bi–Te compounds which have a cross-sectional area of 5×5 mm^2

Sample No.		t_M or t_{Bi-Te} (mm)
Metal	Bi–Te compound	
1a	–	0.5
2a	–	1.2
3a	–	2
4a	–	4
5a	–	6
–	6b	6

the length of metal outside two probes is t_0 at $z = 0$ mm, t_0 is equal to ($t_M - 1$) in a unit of mm for the present case of $t_{Bi-Te} = 6$ mm and $s = 8$ mm. Indeed, when $t_0$was increased from 0.2 mm to 5 mm by changing t_M, the averaged α for M = Cu and Ni was increased by 7.8% in the *p*-type composite, while reversely it was decreased by 2.3% in the *n*-type one. The abrupt increase in α for $t_M < 1$ mm arises from the generation of the barrier thermo-emf near the interface, but some increase and decrease in α for $t_M > 1$ mm result from the difference in the t_0-dependence of the barrier thermo-emf. It indicates that the resultant α depends strongly on the position of leads connected to the metal electrode of a thermoelement. The t_M-dependence of α of M/Bi–Te/M was little changed with the type of metal, although Cu and Ni have an opposite sign in the conduction type. It suggests that the magnitude of the barrier thermo-emf varies significantly with the conduction type of Bi–Te compounds and the thickness t_M of metal rather than the type of metal.

The maximum α of the *p*- and *n*-type Ni/Bi–Te/Ni reached great values of 259 μV/K at $t_M = 6$ mm (corresponding to $t_0 = 5$ mm) and of –276 μV/K at $t_M = 1.2$ mm (corresponding to $t_0 = 0.2$ mm), respectively, which are approximately 26% and 22% higher in absolute value than their intrinsic Seebeck coefficients listed in Table 1. These maximum α values are rather close to 263 and –266 μV/K obtained for the *p*- and *n*-type Cu/Bi–Te/Cu welded with eutectic solder of Pb–Sn [12]. The degrees of enhancement in α for the present composites are smaller than 32% and 30%

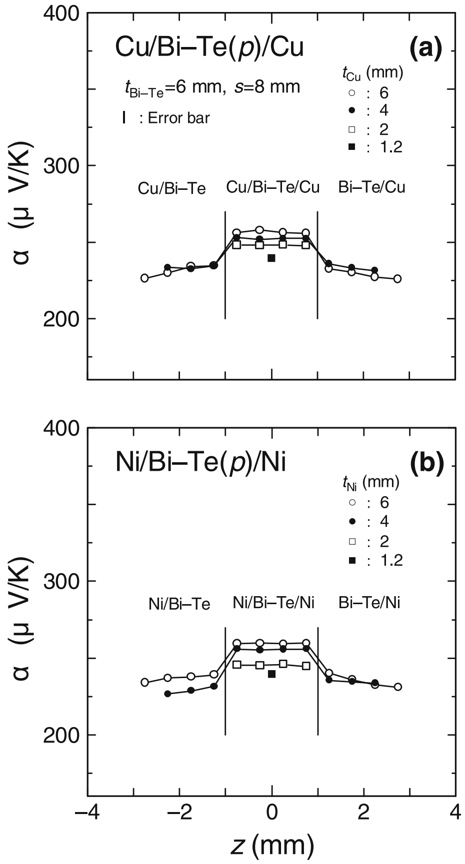

Fig. 4 Resultant α measured as a function of *z* for the *p*-type M/Bi–Te/M (M = Cu and Ni) composites using probes set at an interval of $s = 8$ mm, where $t_M = 1.2$, 2, 4 and 6 mm

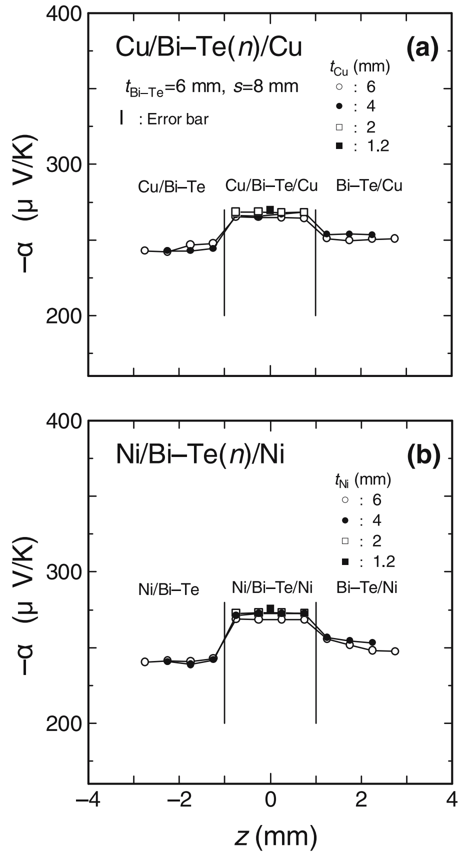

Fig. 5 Resultant α measured as a function of *z* for the *n*-type M/Bi–Te/M (M = Cu and Ni) composites using probes set at an interval of $s = 8$ mm, where $t_M = 1.2$, 2, 4 and 6 mm

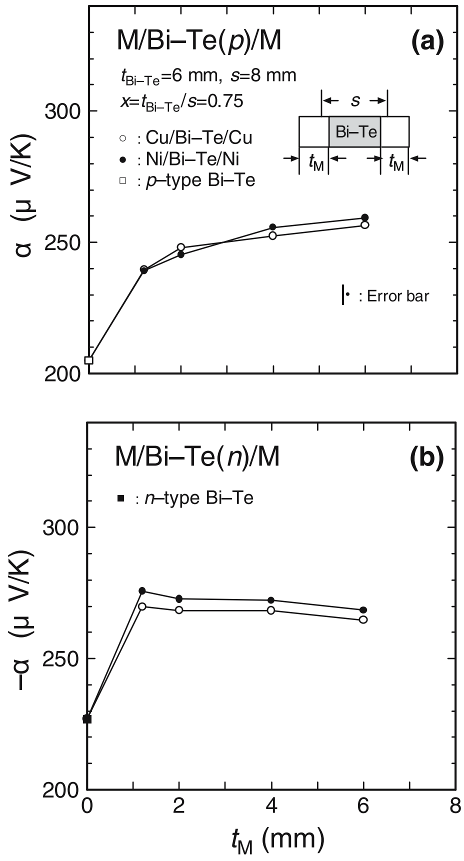

Fig. 6 Dependence of α on the thickness t_M of metals for the *p*- and *n*-type M/Bi–Te/M (M = Cu and Ni) composites, where α is measured with $s = 8$ mm

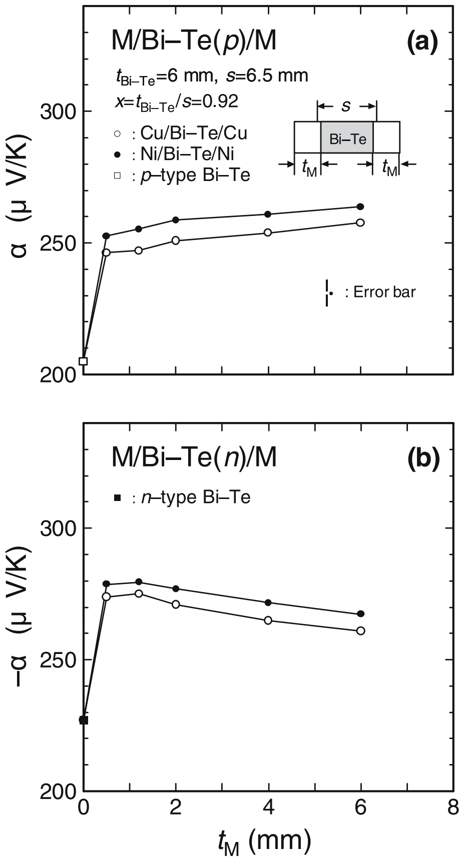

Fig. 7 Dependence of α on the thickness t_M of metals for the *p*- and *n*-type M/Bi–Te/M (M = Cu and Ni) composites, where α is measured with $s = 6.5$ mm at $z = 0$ mm. The thickness t_0 of metal outside two probes corresponds to ($t_M - 0.25$) in a unit of mm

observed at $x = 0.98$ for the welded *p*- and *n*-type Cu/Bi–Te/Cu [12], but are larger than 21% obtained at $x = 0.80$ for the previous welded *n*-type M/Bi/M (M = Cu and Ni) [13]. The phenomenon of enhancement in α has been observed for the welded composites alone, but it was thus found that the enhancement in α due to the barrier thermo-emf of the composites occurs even in touching composites.

$s = 6.5$ mm

Next the resultant α of the *p*- and *n*-type M/Bi–Te/M composites was also measured as a function of t_M, using probes set at an interval of $s = 6.5$ mm, where the sandwiching metals have five different thicknesses of 0.5, 1.2, 2, 4 and 6 mm, as listed in Table 2. In this experiment, α was measured at $z = 0$ mm alone, because s is only a little larger than $t_{\text{Bi–Te}}$ (=6 mm). The present arrangement corresponds to $x = 0.92$. This x is relatively close to $x = 0.98$, giving the maximum α in the *p*- and *n*-type Cu/Bi–Te/Cu composites welded with Pb–Sn [12]. As shown in Fig. 7, the t_M-dependences of the resultant α exhibited tendencies very similar to those obtained with $s = 8$ mm. The resultant α of Cu/Bi–Te/Cu was a little higher in absolute value than that of Ni/Bi–Te/Ni over the whole range of t_M. For the combination of $t_{\text{Bi–Te}} = 6$ mm and $s = 6.5$ mm, t_0 is expressed as $t_0 = (t_M - 0.25)$ in a unit of mm. When t_0 was increased from 0.25 mm to 5.75 mm, the averaged α for M = Cu and Ni was increased by 3.8% in the *p*-type composite, while reversely it was decreased by 4.8% in the *n*-type one. The degree of increase and decrease in α depends on t_0, as in the case of $s = 8$ mm, so that it was found that t_0 also has a significant influence on α, like x. It means that the barrier thermo-emf varies with changes in both t_0 and x. After all, the maximum α values of the *p*- and *n*-type Ni/Bi–Te/Ni composites reached 264 μV/K at $t_M = 6$ mm (corresponding to $t_0 = 5.75$ mm) and –280 μV/K at $t_M = 1.2$ mm (corresponding to $t_0 = 0.95$ mm), respectively, which are nearly equal to those obtained with $s = 8$ mm. It indicates that α is apt to be enhanced when two probe positions are closer to the boundary, i.e., $x(= t_{\text{Bi–Te}}/s)$

is close to 1. In other words, it bears evidence of the fact that the barrier thermo-emf is generated near the interface. This is consistent with the previous results obtained for the welded Cu/Bi–Te/Cu composites [12]. These results suggest that it is necessary to optimize x and t_0, in order to make the resultant α of composites as large as possible.

However, no enhancement in α was observed in the previous *p*- and *n*-type Ag/Bi–Te/Ag composites welded with pure Bi [14]. This is because Bi–Te compound and pure Bi of Ag/Bi–Te/Ag compounds were melted slightly into each other at the interface during welding [14] and they did not form the definite interface fitted to produce a sharp temperature drop at the interface, unlike the welded Cu/Bi–Te/Cu [12] and M/Bi/M [13] composites. As a matter of course, such a phenomenon cannot occur in the touching composites. From these results, therefore, it is expected that when a composite has more definite interfaces, non-equilibrium system carriers at the interface are separated strongly by a sharper temperature drop, resulting in the enhancement of the barrier thermo-emf [10, 11, 15]. From the significant increase in the resultant α of the present composites, it is found that the barrier thermo-emf generated at both interfaces of the present composites is generated in the forward-bias direction.

Dependence of α of the touching composites on time

The resultant α of the *p*- and *n*-type Ni/Bi–Te/Ni composites was measured as a function of time t up to 90 min, in order to investigate whether α changes with time. The measurement was made with $s = 8$ mm on the *p*-type Ni/Bi–Te/Ni of $t_M = 6$ mm and with $s = 6.5$ mm on the *n*-type Ni/Bi–Te/Ni of $t_M = 1.2$ mm. As shown in Fig. 8, the observed α of these composites remained almost constant up to 90 min even in either type of conduction and was surprisingly steady. It indicates that a high and steady thermo-emf is obtained even in touching composites.

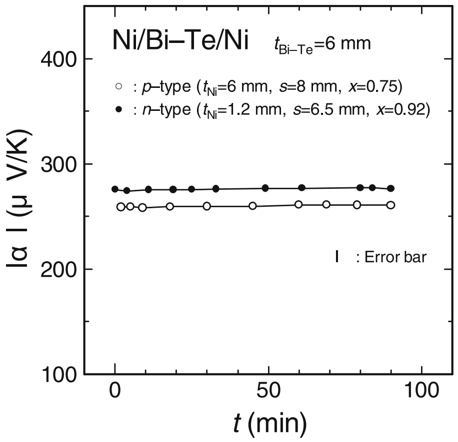

Fig. 8 Time dependence of α for the *p*-type Ni/Bi–Te/Ni composite with $t_M = 6$ mm and *n*-type Ni/Bi–Te/Ni composite with $t_M = 1.2$ mm, where α of the former and latter ones were measured with $s = 8$ mm and 6.5 mm, respectively

Summary and conclusion

The resultant Seebeck coefficients α of the touching *p*- and *n*-type M/Bi–Te/M (M = Cu and Ni) composites were measured as a function of z at a scan step of 0.5 mm using thermocouples set at three different intervals of $s = 4$, 6.5 and 8 mm, where s is the interval between two probes and z is the distance from the center of Bi–Te compound to the middle of two thermocouples. Bi–Te compounds have a constant thickness of $t_{Bi-Te} = 6$ mm but the thickness t_M of both end metals was varied from 0.5 mm to 6 mm. The touching composites were compacted tightly at a force of about 10 N by a ratchet. When two probes were placed on Bi–Te compound, the resultant α agreed well with the intrinsic one, while when two probes are placed on both end metals, it was enhanced significantly, like the welded composites, particularly when $x(= t_{Bi-Te}/s)$ is close to 1. This significant enhancement in α is attributed to the contribution from the barrier thermo-emf generated in the forward-bias direction. When the thickness t_0 of metal outside two probes set at $s = 6.5$ mm was increased from 0.25 mm to 5.75 mm, the averaged α for M = Cu and Ni was increased by 3.8% in the *p*-type composite, while reversely it was decreased by 4.8% in the *n*-type one. It was thus found that x and t_0 have a significant influence on the resultant α. The maximum α observed with $s = 6.5$ mm for the *p*- and *n*-type Ni/Bi–Te/Ni composites reached great values of 264 μV/K at $t_M = 6$ mm (corresponding to $t_0 = 5.75$ mm) and − 280 μV/K at $t_M = 1.2$ mm (corresponding to $t_0 = 0.95$ mm), respectively, which are 29% and 23% larger in absolute value than their intrinsic α values and are roughly close to 263 μV/K and −266 μV/K obtained previously for the welded *p*- and *n*-type Cu/Bi–Te/Cu composites. The maximum α of these composites was barely changed with time. A high and steady thermo-emf is thus found to be obtained even in touching composites. From these results, the position of leads connected to the metal electrode of a thermoelement was found to be very important for the enhancement in the resultant α. Of course, such a high-performance module is available for a generator, not for a Peltier module.

Finally, it is desired strongly that the mechanism for the generation of the barrier thermo-emf would be investigated hereafter, in order to achieve further enhancement in α of composites.

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