J MATER SCI **41** (2006) 3089–3095

Enhancement of the thermoelectric power factor in Ag/Bi-Te/Ag composite devices

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The resultant thermoelectric properties of the *p*- and *n*-type Ag/Bi-Te/Ag composite devices welded with pure Bi were measured at 298 K as a function of relative thickness of x, where x is the ratio of thickness of Bi-Te compound to the interval between two thermocouples and the chemical compositions of the *p*- and *n*-type Bi-Te compounds used here are $(Bi_{0.25}Sb_{0.75})_2Te_3$ and $Bi_2(Te_{0.94}Se_{0.06})_3$, respectively. Consequently, the electrical resistivities ρ of the *p*- and *n*-type Ag/Bi-Te/Ag devices increased linearly with an increase of x, while the Seebeck coefficients α were enhanced significantly in the range from $x = 0.03$ to 0.10, so that their observed P values have a large local maximum at $x = 0.06$. The x-dependence of P values was found to be explained roughly with the simple model proposed here when some reduction in the thermal conductivity κ of Ag and Bi was taken into the calculation. The maximum P of the *p*- and *n*-type Ag/Bi-Te/Ag devices reached extremely large values of 27.8 and 88.3 mW/K^{2}m, which are higher than 25.7 mW/K^{2}m obtained for the previous *n*-type Ni/Bi/Cu device.
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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 power factors $P = \alpha^2/\rho$, where α is the Seebeck coefficient and ρ is the electrical resistivity. P is given in terms of the material's electrical transport properties, and it enters the thermoelectric figure of merit $Z{=}P/\kappa$, where κ is the total thermal conductivity which contains both lattice and electronic contributions. Thus, P provides a measure of the quality of a material for cooling [6].

Recently, the resultant P of two-component composite device was calculated by Bergman and Fel [7], who predicted theoretically that the resultant P can be sometimes be greater than the power factors of two different pure components, by employing the model based on the classical continuum linear transport theory. Most recently, such an enhancement in P has been observed by the present authors in macroscopic composite devices, in which the maximum P value reached a large value of 25.7 mW/K^{2}m in the *n*-type Ni/Bi/Cu device [8].

Theoretically, the resultant maximum P is enhanced significantly as the difference between the thermal conductivities of a metal with a low electrical conductivity and a sandwiched thermoelectric with a high Seebeck coefficient increases. Therefore, P values of Ag/Bi-Te/Ag composite devices are expected to become larger than those of Ni/Bi/Cu devices in which pure Bi is employed as a thermoelectric, since the thermoelectric Bi-Te compounds have a thermal conductivity lower and a Seebeck coefficient higher than Bi, and Ag has a thermal conductivity higher and an electrical resistivity lower than Cu or Ni.

In this paper, the dependence of the resultant P on the relative thickness of Bi-Te compounds was investigated experimentally for the *p*- and *n*-type Ag/Bi-Te/Ag composite devices welded with pure Bi. The theoretical resultant P of the composite device with a sandwich structure was calculated as a function of relative thickness of Bi-Te compound by treating it as an electrical and thermal circuit, including the thermoelectric contribution from relatively thin Bi layers, and the dependence of P values on the relative thickness of Bi-Te compounds was found to be explained roughly with the simple model proposed here. The observed P values were com-

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DOI: 10.1007/s10853-006-2621-z

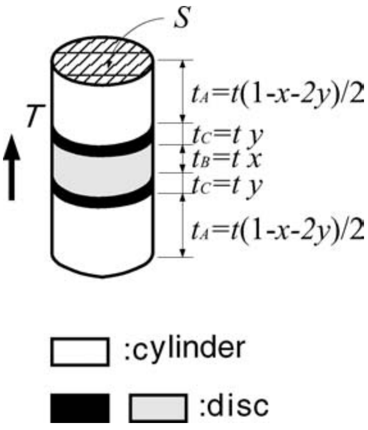

Figure 1 Composite thermoelectric device (CTD) with a sandwich structure (A/C/B/C/A) in which a disc of thermoelectric material B is sandwiched directly between two discs of materials C and it is further sandwiched between two cylinders of material A. The direction of the temperature gradient ΔT is along the cylindrical axis of the device.

pared with the power factors calculated using our simple model.

The purpose of this paper is to investigate to what degree the thermoelectric power factors P of the p- and n-type Ag/Bi-Te/Ag composite devices are enhanced by employing the p-and n-type Bi-Te compounds instead of a thermoelectric Bi and to confirm whether the observed P values can be explained with our simple model.

2. Calculation and experiments

2.1. Calculations of electrical resistivity, Seebeck coefficient and power factor of a composite device

Let us consider a component 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 resultant P for CTD by treating CTD as an electrical and thermal circuit, in which the direction of the temperature gradient is along the cylindrical axis [8]. 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. It was assumed here that the scattering of carriers and phonons never occurs at the interface between discs and cylinders. 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

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

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

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

where $b_1 = \rho_A/\rho_B$ and $b_2 = \rho_C/\rho_B$. 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

$$\frac{\Delta T_A}{\Delta T_B} = \frac{t_A\kappa_B}{t_B\kappa_A} = \frac{(1-x-2y)}{2c_1 x} \tag{3}$$

and

$$\frac{\Delta T_C}{\Delta T_B} = \frac{t_C\kappa_B}{t_B\kappa_C} = \frac{y}{c_2 x}, \tag{4}$$

where $c_1 = \kappa_A/\kappa_B$ and $c_2 = \kappa_C/\kappa_B$. The total temperature difference ΔT between both ends of CTD is given by

$$\Delta T = 2\Delta T_A + \Delta T_B + 2\Delta T_C. \tag{5}$$

By substituting Eqation 3 and 4 into Equations 5, 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

$$\frac{\Delta T_B}{\Delta T} = \frac{c_1 c_2 x}{c_2(1-x-2y) + 2c_1 y + c_1 c_2 x}, \tag{6}$$

and

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

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

$$\Delta V = 2\Delta T_A\alpha_A + \Delta T_B\alpha_B + 2\Delta_C\alpha_C. \tag{8}$$

Therefore, the overall Seebeck coefficient α is expressed as

$$\begin{aligned}\alpha &= \frac{\Delta V}{\Delta T} \\ &= \alpha_B\frac{a_1 c_2(1-x-2y) + 2a_2 c_1 y + c_1 c_2 x}{c_2(1-x-2y) + 2c_1 y + c_1 c_2 x}\end{aligned} \tag{9}$$

using Equations 3–8, where $a_1 = \alpha_A/\alpha_B$ and $a_2 = \alpha_C/\alpha_B$. Substituting Equations 2 and 9 into the equation $P = \alpha^2/\rho$, the resultant P is expressed using P_B of the thermoelectric material as

$$\frac{P}{P_B} = \left\{\frac{a_1c_2(1-x-2y)+2a_2c_1y+c_1c_2x}{c_2(1-x-2y)+2c_1y+c_1c_2x}\right\}^2 \times \frac{1}{\{x+b_1(1-x-2y)+2b_2y\}}, \quad (10)$$

where $P_B = {\alpha_B}^2/\rho_B$. Of course, Equation 10 reduces to $P = P_B$ if $x = 1$ and $y = 0$ and to $P = P_C$ if $x = 0$ and $y = 1/2$.

It has already been demonstrated in our previous paper [8] that Equation 10 has a local maximum greater than 1 at optimum parameters, which is greater than the maximum among the three different components. The resultant maximum P tends to increase significantly as the ratio of the thermal conductivity of a metal with a low electrical resistivity to that of a thermoelectric material with a high Seebeck coefficient becomes large, but the thickness of a thermoelectric disc then tends to become relatively thinner. For a composite device composed of two different types of materials, it was proved by Bergman and Fel [7] that the power factor is enhanced markedly at an optimum volume fraction, under specified conditions. However, the same will also be demonstrated theoretically by using the simple model that the power factor of sandwiched composite devices can be enhanced significantly, even in the composite device composed of three different types of materials.

2.2. Sample preparation

The ingots of 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 0.060 wt% Te and 0.068 wt% I were prepared by the Bridgman method, using purer Bi granules of 99.999% and pure Sb, Te, Se and I of 99.99% as starting materials. After the ingots were pulverized to granules, they were charged into a glass tube of an inner diameter slightly smaller than 5 mm and melted in an evacuated glass tube by an induction heating to make a homogeneous melt without segregation. The resulting cylindrical p- and n-type ingots were consisted of relatively fine grains of approximately 0.3 mm on average. The cylindrical ingots of pure Bi were also prepared by the same method as that of the Bi-Te compound after the Bridgman process and were cut into discs with a thickness of 1 mm.

The Ag/Bi-Te/Ag composite devices were prepared by welding with Bi of 99.99%, using Ag of 99.99% and the p- and n-type Bi-Te compounds which have cylindrical shapes with a diameter slightly smaller than 5 mm. The thickness of Bi-Te compounds was determined so that the Bi-Te compounds sandwiched between two Ag cylinders have various thicknesses but the total length of composite devices becomes 20 mm. After both end surfaces of Bi discs, Ag cylinders and Bi-Te compounds were polished mechanically by the lapping method to make flat the welded surfaces, a set of Ag, Bi, Bi-Te compound, Bi and Ag was put in a glass tube of an inner diameter φ 5 mm so that the materials A, B and C described earlier correspond to Ag, Bi-Te compound and Bi, respectively. Since pure Bi has a very low melting point of 544 K [9], as compared to those of Ag and Bi-Te compounds, Bi was first melted in a glass tube by an induction heating. While Bi is melted, as shown in Fig. 2, cylindrical Bi-Te compound and Ag metal were welded with Bi by compressing both ends of two Ag cylinders at a constant force of 2 N using two iron rods, so that most of molten Bi is sunk into a narrow interval between a glass tube and a cylindrical Ag or Bi-Te compound. After a welded cylinder was naturally cooled to room temperature, it was ejected out of a glass tube using an iron rod. Microphotographs of welded boundaries in the p-and n-type Bi-Te compounds are shown in Fig. 3. The average grain sizes of the p- and n-type Bi-Te compounds after welding remained almost unchanged before and after welding. The thicknesses of Bi-Te compounds and Bi used as an adhesive were measured after polishing the surface along the cylindrical axis of welded devices, so that the boundary between Ag and Bi-Te compounds becomes clear, as shown in Fig. 3. Af-

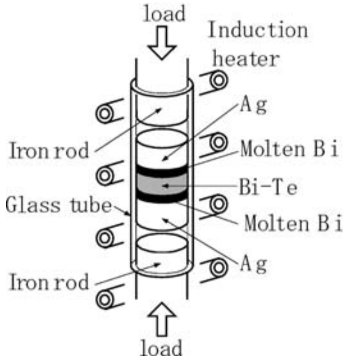

Figure 2 Fabrication method of composite devices welded with pure Bi.

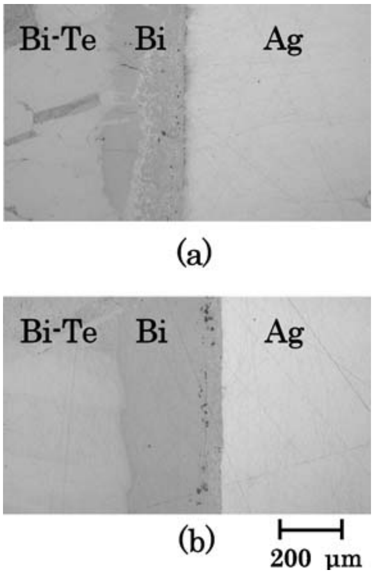

Figure 3 Microphotographs of welded boundaries in the p- type (a) and n-type (b) Ag/Bi-Te/Ag devices.

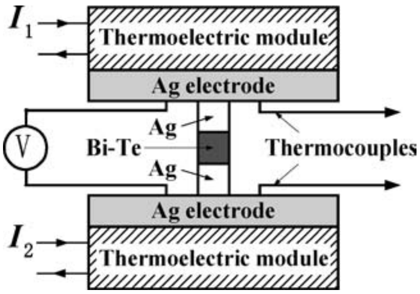

Figure 4 Schematic configuration for measurements of the Seebeck coefficient α of composite devices. One end was heated by flowing the electrical current I_1 or I_2 through a thermoelectric module to produce the temperature differences of $\Delta T = \pm 3$ K and another one was then maintained at room temperature. The thermocouples and leads on Ag plates are about 1 mm distant from the top and bottom edges of the specimen.

ter polishing, there were some pores in Bi layer near Ag metal, but no crack was detected at the boundaries of all devices. As shown in the figure, the average thickness of Bi layer was then equal to or less than approximately 0.2 mm in any device, which corresponds to $y = 0.01$ from the relation $y = t_{Bi}/t$.

In order to observe the intrinsic thermoelectric properties of materials used here, they were subjected to Seebeck coefficient and electrical resistivity measurements (Sinku-Riko, Inc., Model ZEM-1). The Seebeck coefficient α was measured at 298 K with an accuracy of 3% by the conventional technique, using two alumel-chromel thermocouples set at an interval of 8 mm, with the temperature difference of about 5 K. The electrical resistivity ρ was measured concurrently with an accuracy of 1% by the four-probe method.

Subsequently, the Seebeck coefficient α of composite devices of a length of 20 mm was measured using an apparatus schematically shown in Fig. 4. As the present apparatus is available with any length of device, it is easy to observe α value of such a long composite device. Particularly when P has a local maximum at small x, it is required to prepare a device with a very thin Bi disc as long as the length of a device is short. Since it is very difficult to thin a very brittle Bi-Te disc extremely, we fabricated long devices with a total length of 20 mm. Ag plates with a lower ρ were used as electrodes to measure more precisely the electrical resistivity of a device with a low ρ. Either of both ends was heated alternatively to produce the temperature differences of $\Delta T = \pm 3$ K. One end was heated from 298 to 301 K by flowing the electrical current I_1 or I_2 through a thermoelectric module and another end was then maintained at 298 K, owing to a large heat capacity of a module with a volume of $50 \times 50 \times 5$ mm^3. The temperature difference ΔT of both ends was measured with an accuracy of 0.1 K by two thin copper-constantan thermocouples with a thickness of 0.1 mm. The α was estimated using the relation $\alpha = \Delta V/\Delta T$ with an accuracy of 3% or less. During these measurements, a composite device was put between two Ag plates under a constant force of 29.4 N, so that a device contacts tightly with two Ag plates.

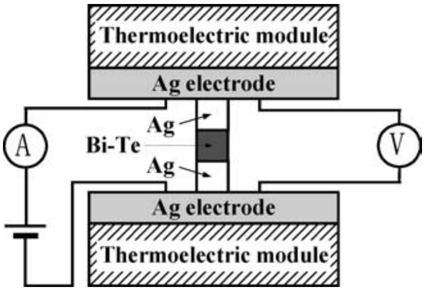

Figure 5 Schematic configuration for measurement of the electrical resistivity ρ of composite devices. When the constant current I flows between two Ag plates, the voltage drop V appeared on two Ag plates was measured.

The schematic configuration for measurement of the electrical resistivity ρ of composite devices is shown in Fig. 5. When the constant current I flows between two Ag plates, the voltage drop V appeared on two plates was measured at 298 K under the same pressure as that compacted during the measurement of α.

As well-known, $\sigma (=1/\rho)$ and κ of the Bi-Te compounds have a strong anisotropy, that is, $\sigma_\perp$ and $\kappa_\perp$ are 2–3 times larger than $\sigma_{||}$ and $\kappa_{||}$, where the $\perp$ and $||$ denote directions perpendicular and parallel to the c axis, respectively [10, 11]. However, there is little crystallographic anisotropy in α [10, 11]. The power factor of the composite devices, therefore, may change with the difference in the degree of alignment of the c plane of Bi-Te compounds. For this reason, X-ray diffraction (XRD) using Cu-K$_\alpha$ radiation (λ =1.5418 Å) was made on the powdered and welded Bi-Te compounds, in order to investigate whether the welded Bi-Te compounds are an isotropic polycrystalline.

3. Results and discussion

3.1. Dependence of the resultant ρ and α on relative thickness x of Bi-Te

The intrinsic thermoelectric properties of Ag, Bi and the p- and n-type Bi-Te compounds used here are listed in Table I. The measured ρ values of pure Ag and Bi are in good agreement with the previous data [12, 13]. As shown in Fig. 6, XRD measurement was made on the cross-section of some welded Bi-Te compounds ($x = 0.3$ to 0.8) and on their powders, in order to investigate whether the welded compounds are an isotropic polycrystalline. As a result, the welded p- and n-type Bi-Te compounds were found to be almost an isotropic polycrystalline from the fact that XRD patterns of powdered and welded compounds are similar to each other. The experimental α ($=-70$ μV/K) of polycrystalline Bi is very close to -68.3 μV/K calculated as the mean value using the equation $\alpha = (\alpha_{33} + 2\alpha_{11})/3$, where α_{33} and α_{11} were Seebeck coefficients measured at 300 K along the trigonal and binary directions of single-crystal Bi [13].

The resultants ρ and α of the p- and n-type Ag/Bi-Te/Ag devices were measured at 298 K as a function of x, where x is the ratio of thickness of a disc Bi-Te to an interval of 20 mm. The measured values were compared with the cal-

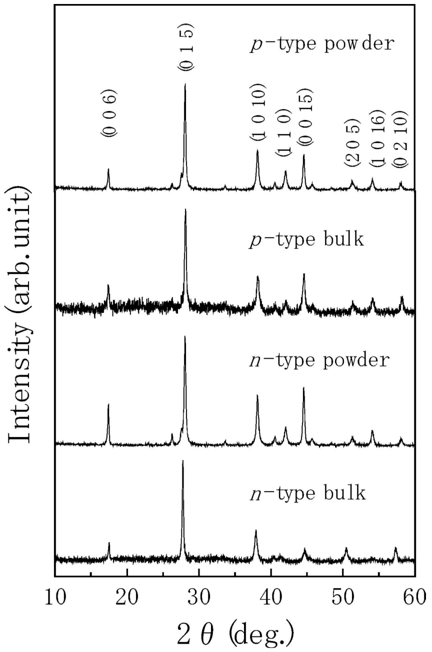

Figure 6 X-ray diffraction patterns of the powdered and welded p- and n-type Bi-Te compounds.

culated ρ and α by treating these devices as an electrical and thermal circuit, including the thermoelectric contribution from thin Bi layers. No significant difference in ρ and α occurred in any device when the direction of the temperature gradient was reversed. As shown in Fig. 7, the observed ρ values of the p- and n-type Ag/Bi-Te/Ag devices increased linearly with an increase of x and fell roughly on the dashed curves $\rho(x)$ calculated from Equation 2 using $y = 0.01$ and the experimental values (see Table I). To the contrary, the observed α values of their composite devices increase abruptly with an increase of x and tend to saturate at $x \fallingdotseq 0.3$ to approximately 200 μV/K in the p-type device and to approximately -230 μV/K in the n-type one. However, the observed α values of the p- and n-type composite devices scarcely fall on the solid curves $\alpha(x)$ calculated from Equation 9 using $y = 0$ and the experimental values, while when calculated using $y = 0.01$, they fell on the dotted curves $\alpha(x)$ rather than on the dashed ones, where the dotted ones are calculated using a low κ_{Ag} of 200 W/mK and a low κ_{Bi} of 2.8 W/mK for the p-type device or a low κ_{Bi} of 3.8 W/mK for the n-type one. These κ values used for the calculation are 35–48% of the experimental κ values (see Table I). The reason that the observed α values coincided with the dotted curves in the small x region is considered as follows. A relatively long Ag cylinder (corresponding to small x) with a high thermal conductivity is apt to generate the thermal radiation during the thermal conduction through a device, so that κ_{Ag} is reduced apparently to make small the difference between κ_{Ag} and $\kappa_{\mathrm{Bi-Te}}$. Such a lowering in κ_{Bi} in the small x region may arise from the diffusion of Ag or Te atom into pure Bi layer during the welding process. This tendency should become prominent as the thickness of Bi-Te discs becomes thinner.

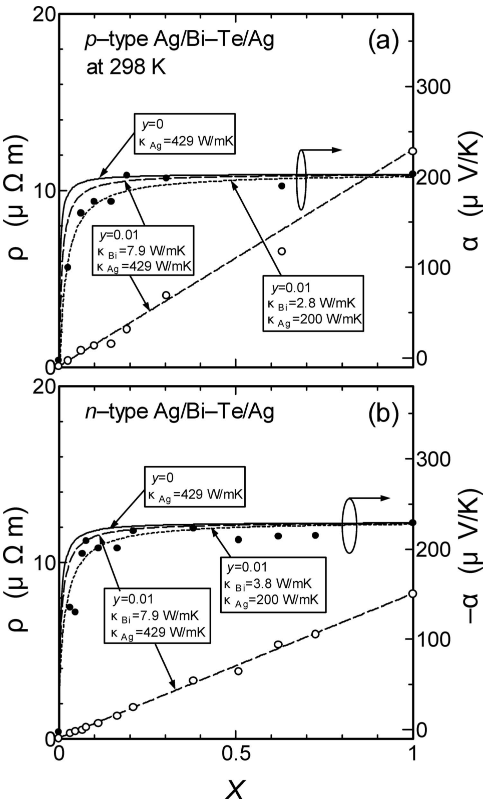

Figure 7 Resultants ρ and α as a function of x for the p-type (a) and n-type (b) Ag/Bi-Te/Ag composite devices welded with pure Bi. The theoretical curves of $\rho(x)$ and $\alpha(x)$ were calculated from Equations 2 and 9, by using the experimental values (see Table I) or by assuming some reduction in κ_{Ag} and κ_{Bi}.

The calculated α values tend to approach a constant value with an increase of x, independently of values used here for various parameters. However, the observed α values of these Ag/Bi-Te/Ag devices never exceeded those of Bi-Te compounds, although the α values of M/Bi/N (M and Ni = Cu or Ni) devices were more than that of a thermoelectric pure Bi above $x = 0.3$ [8]. The fact that α values of the present composite devices were not enhanced at all may be attributed to the presence of a thin Bi layer lying between Bi-Te compounds and Ag metal. Because a thin Bi with a low thermal conduction much lower than κ_{Ag} acts to obstruct the thermal conduction through a device, resulting in a substantial reduction of the temperature gradient ΔT generated in Bi-Te compounds.

3.2. Dependence of the resultant *P* on relative thickness *x* of Bi-Te

The resultant P was plotted as a function of x for the p- and n-type Ag/Bi-Te/Ag devices in Fig. 8. The observed P values have a local maximum at $x \fallingdotseq 0.06$ in both p- and n-type composite devices. The maximum P of the n-type device was approximately 3 times larger than that of the p-type one. This is because α values of the p-type Bi-Te compound and the n-type pure Bi are opposite in sign, leading to a decrease in the resultant α of a composite

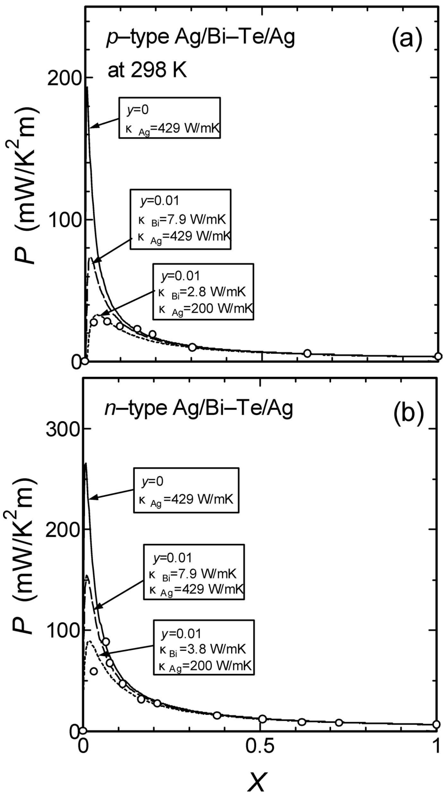

Figure 8 Resultant P as a function of x for the p-type (a) and n-type (b) Ag/Bi-Te/Ag composite devices welded with pure Bi. The theoretical curves of $P(x)$ were calculated from Equation 10, by using the experimental values (see Table I) or by assuming some reduction in κ_{Ag} and κ_{Bi}.

device. The solid curves denote P values calculated from Equation 10 using $y = 0$ and the experimental values, as listed in Table I. The observed P values of the p- and n-type devices agree well with the solid curves above $x = 0.15$, while below $x = 0.15$, they are much smaller than the solid ones, as shown in Fig. 8. However, the observed P values of the p-type device rather than the n-type one fell well on the dotted curves all over x, as in the case of α and ρ values, where the dotted curves were calculated as before, using $y = 0.01$, a low κ_{Ag} of 200 W/mK and a low κ_{Bi} of 2.8 W/mK for the p-type device or a low κ_{Bi} of 3.8 W/mK for the n-type one. That is, the x–value giving a theoretical maximum P in the n-type device is much smaller than that doing an experimental maximum P. Probably this disagreement may also come from some change in the thermoelectric properties of Bi and Bi-Te compound near the welded boundary. It is thus found that a thin Bi layer with a lowered κ also acts to reduce significantly P values of composite devices. When the thickness of the welded Bi layer became thinner, therefore, the resultant P of composite devices would be enhanced significantly, particularly in the p-type device, and would approach to the ideal solid curves, as shown in Fig. 8.

When the substantial reduction in κ values of Ag cylinder and welded Bi layer was taken into the calculation, the observed P values of the composite devices tend to coincide with the calculated curves. As expected theoretically, the maximum P of the p- and n-type Ag/Bi-Te/Ag devices reached extremely large values of 27.8 and 88.3 mW/K^{2}m, which are higher than 25.7 mW/K^{2}m obtained for the previous n-type Ni/Bi/Cu device [8] and are much greater than 5.7 and 6.6 mW/K^{2}m of the high- performance bulk p- and n-type bismuth-telluride compounds [14, 15].

4. Summary and conclusion

The resultant thermoelectric power factors P of the p and n-type Ag/Bi-Te/Ag devices were measured at 298 K as a function of relative thickness of x, where the p- and n-type Bi-Te compounds used here are $(\mathrm{Bi}_{0.25}\mathrm{Sb}_{0.75})_2\mathrm{Te}_3$ and $\mathrm{Bi}_2(\mathrm{Te}_{0.94}\mathrm{Se}_{0.06})_3$, respectively, and x is the ratio of thickness of Bi-Te compound to the interval between two thermocouples which is separated by a distance of 20 mm. The electrical resistivities ρ of Ag/Bi-Te/Ag composite devices increase linearly with an increase of x, while the Seebeck coefficients α increase significantly with increasing x in the range from $x = 0.03$ to 0.10 and tend to saturate above $x = 0.3$. However, α values of Ag/Bi-Te/Ag devices never exceeded those of Bi-Te compounds, unlike M/Bi/N (M and N = Cu or Ni) devices, and it may be attributed to the presence of Bi layer lying between Bi-Te compound and Ag metal. After all, the observed P values of the p and n-type Ag/Bi-Te/Ag devices have a large local maximum at x=0.06. The x-dependence of P values was found to be explained roughly by our simple model when some reduction in κ values of pure Ag and Bi layer was taken into the calculation. The maximum P of the p- and n-type Ag/Bi-Te/Ag devices reached extremely large values of 27.8 and 88.3 mW/K^{2}m, which are higher than 25.7 mW/K^{2}m obtained for the previous n-type Ni/Bi/Cu device.

It was thus found that the thermoelectric power factor of a composite device is enhanced extremely when a relatively thin thermoelectric material with a high Seebeck coefficient was sandwiched between two metals with both a low electrical resistivity and a high thermal conductivity.

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Received 7 March 2005
and accepted 27 May 2005