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Journal of Alloys and Compounds 434–435 (2007) 710–713

Journal of ALLOYS AND COMPOUNDS

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Thermoelectric properties of gas atomized p-type Sb_2Te_3–25% Bi_2Te_3 alloys

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Abstract

In order to investigate an effect of rapid solidification on the thermoelectric performance and materials properties, p-type Bi_2Te_3–Sb_2Te_3 thermoelectric alloy doped with 4 wt.% Te was synthesized using gas atomization and sintering processes. The gas atomized alloy presented a homogeneous distribution of Te, Bi and Sb. Bending strength was also improved compared with the alloy prepared by conventional casting process. Variation of thermoelectric properties such as Seebeck coefficient, electrical conductivity, thermal conductivity and Hall properties were analyzed as a function of the initial powder size, annealing treatment and sintering temperature.

Keywords: p-Type Bi_2Te_3–Sb_2Te_3; Thermoelectric properties; Gas atomization; Powder metallurgy

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1. Introduction

It is known that the intrinsic low strength and uneven thermoelectric performance of directionally grown p-type Sb_2Te_3–Bi_2Te_3 alloys can be improved with fine and homogeneous distribution of thermoelectric phases formed during rapid solidification process (RSP) [1–3]. The RSP is also effective for suppressing the anisotropy in the crystallographic orientation and thermoelectric performance apparently due to the unit cell consisting of a large ratio of *c*-axis to *a*-axis [4]. However, little investigation of the gas atomized Bi_2Te_3 type alloy has been reported on the mechanical and thermoelectric properties.

In the present study, p-type Sb_2Te_3–25% Bi_2Te_3 doped with an excess of 4 wt.% Te powders were prepared using gas atomization, a typical rapid solidification process for mass production [5,6], and consolidated via sintering. The mechanical properties and thermoelectric properties such as thermoelectric power, electric resistivity and figure of merits were evaluated as a function of the powder size, sintering temperature and annealing.

2. Experimental

Sb_2Te_3–25% Bi_2Te_3 powders doped with an excess of 4 wt.% Te were prepared using a high pressure gas atomizer. Each powder of 33–90 μm and 91–355 μm were degassed under H_2 and pressed under 400 MPa, to a cold density of 6.4 g/cm^3. The cold pressed sample was sintered in the pyrex tube at temperatures of 400 °C, 450 °C and 500 °C for 50 min, followed by annealing at 380 °C for 1 h under pressure of about 0.133 Pa.

Standard four points probe method and Van der Pauw method (5 kG, 50 mA) were used to measure the electrical resistivity and the room temperature Hall coefficient and Hall mobility, respectively. The latter value was measured by an ac technique with a constant magnetic field in the range of 0.5–0.9 T. Thermoelectric power (σ) was determined by measuring the temperature and electric potential difference between each end of the specimen [4], in which the temperature along the sample varied by 0–10 K. Thermal conductivity was measured using Harman method at 1.33×10^{-3} Pa to minimize the thermal conduction through convection [7]. These data were used to determine carrier concentration, carrier mobility and the thermoelectric figure of merit.

The strength of sintered body was obtained by three-point bending tests. For the microstructural analysis, Scanning Electron Microscope (SEM, JEOL 5410) and Energy Dispersive X-ray Spectroscope (EDS, Oxford 3.0) were used. The crystal structures in both ribbon and bulk were characterized by an X-ray diffractometer (XRD, Siemens) using monochromatic Cu-Kα radiation. ICP (ICPS-1000III, Shimadzu) was used to analyze the composition variation.

3. Results and discussion

Gas atomized and sintered p-type Sb_2Te_3–25% Bi_2Te_3 alloy doped with 4 wt.% Te consists of rhombohedral Bi_2Te_3–Sb_2Te_3 compounds characterized using X-ray diffraction as shown in Fig. 1. RSP might be effective to form thermoelectric phases of Bi_2Te_3 and Sb_2Te_3 among various types of intermetallic compounds formed during the equilibrium solidification [8]. Fig. 2 shows SEM image (upper left) and EDS elemental maps (Te, Sb and Bi) of powders as atomized, in which no segregation of any Te, Sb and Bi is found. Densities were measured to be 6.41, 6.56 and 5.38 g/cm^3 as the sintering temperatures increased from

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doi:10.1016/j.jallcom.2006.08.251

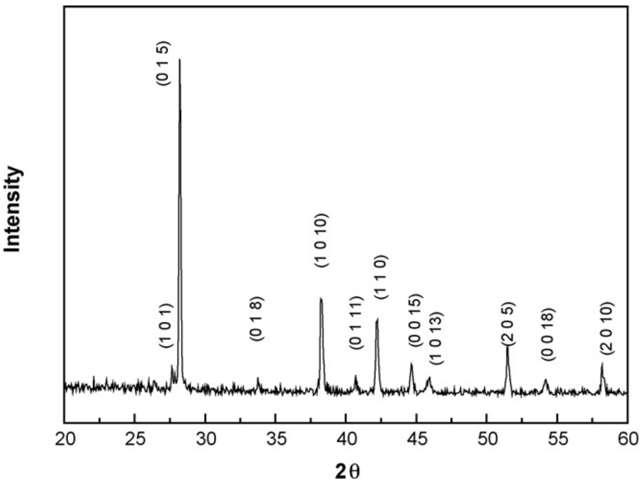

Fig. 1. XRD diffraction pattern of gas atomized p-type Sb_2Te_3–25% Bi_2Te_3 alloy doped with 4 wt.% Te, indicating formation of Sb_2Te_3–Bi_2Te_3 phases.

400 °C to 450 °C and 500 °C, respectively. The lower densities at 400 °C and 500 °C than at 450 °C might be due to an incomplete reaction and formation of pores by Te evaporation during the sintering [8]. The evaporation was identified from ICP data (Table 1). With increasing sintering temperature, the amount of Te became low, whereas Bi and Sb increased. The loss of Te was maximum (4.14 wt.%) at temperatures between 450 °C and 500 °C, while the reduction of less than 1 wt.% occurred at the lower temperature range.

In order to know the effect of RSP on the mechanical properties, bending tests were applied to both alloys conventionally cast and gas atomized (sintered at 450 °C). Since the strength is 19.6 MPa for the cast specimen, 45.9 MPa from the RSP is quite high enough to substitute the conventional process. This is possibly due to the homogeneous and fine microstructures obtained by the gas atomization.

Fig. 3 shows Seebeck coefficients (α) of the sintered p-type Sb_2Te_3–25% Bi_2Te_3 materials as a function of the initial powder size, annealing treatment and sintering temperature. α was increased by annealing the finer powders, in which the highest

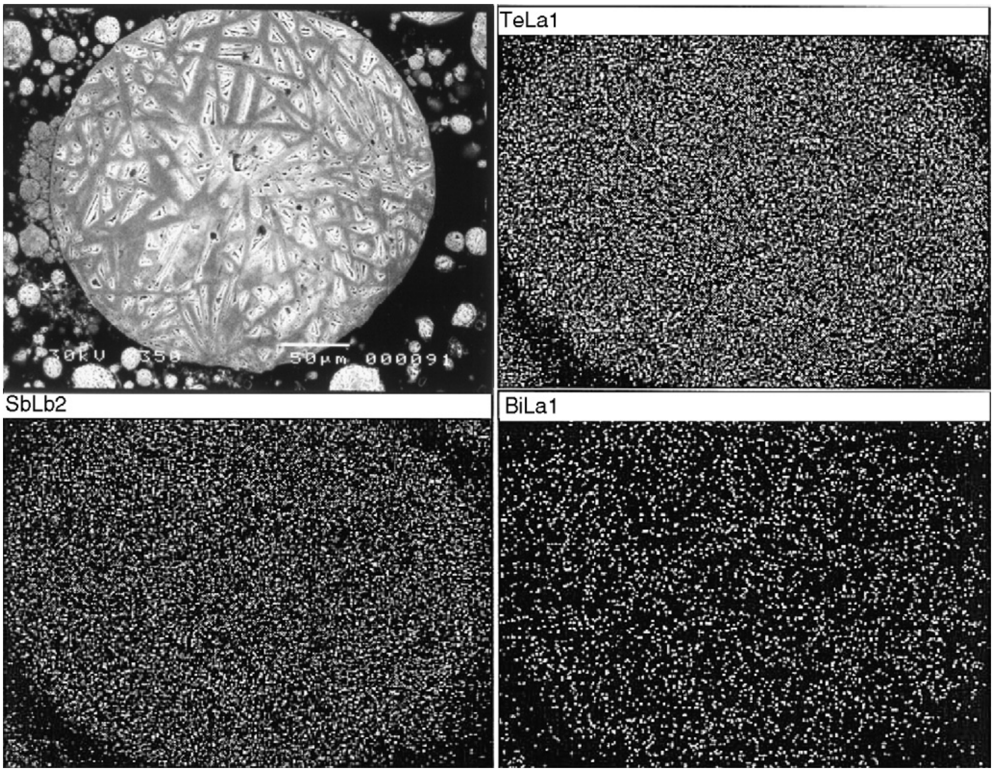

Fig. 2. Secondary electron image (upper left) and the elemental maps of Te, Sb and Bi in gas atomized p-type alloy powder.

Table 1
Composition of p-type Sb_2Te_3–25% Bi_2Te_3 alloy doped with 4 wt.% Te atomized and sintered

	Before sintering	Sintering (400 °C)	Sintering (450 °C)	Sintering (500 °C)	Annealing after sintering at 450 °C
Bi	14.45	14.50	14.60	16.02	14.73
Te	58.47	57.96	57.19	53.05	56.08
Sb	27.05	28.11	28.11	30.81	29.10
Total	99.97	99.92	99.97	99.88	99.91

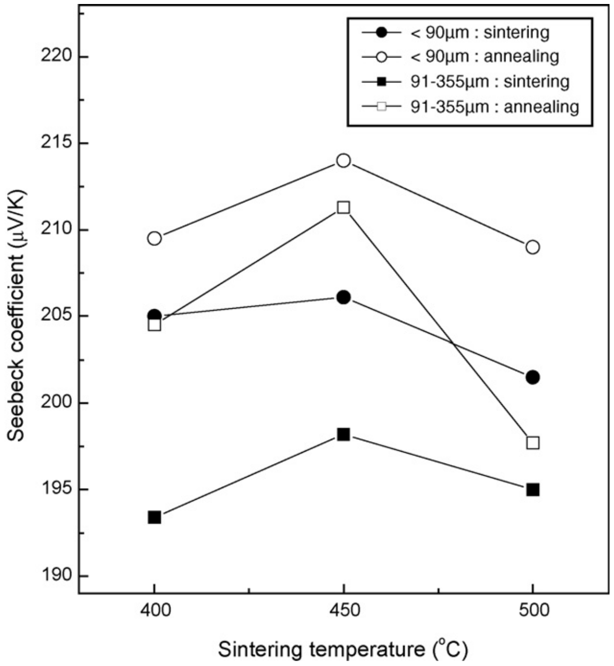

Fig. 3. Seebeck coefficients (α) measured as a function of initial powder size, annealing (380 °C) treatment and sintering temperature.

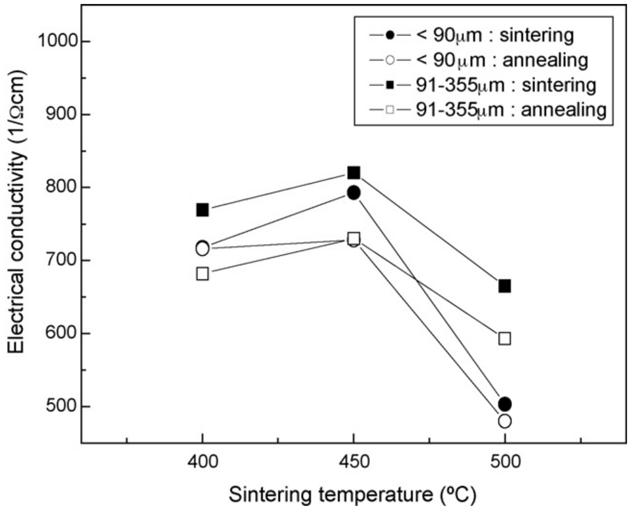

Fig. 4. Electrical conductivity (σ) with the sintering temperature, powder size and annealing (380 °C) treatment.

value of 212 μV/K was obtained by sintering the powders (33–90 μm) at 450 °C, followed by annealing at 380 °C.

Considering the sintering temperature, the increase of α between 400 °C and 450 °C and the decrease at 500 °C is due to the density as well as Te evaporation during the sintering. The former effect may correspond to good densification improving the thermoelectric contact. The latter factor is related to the carrier concentration (Table 1). During melting of the p-type Bi_2Te_3–Sb_2Te_3 alloys, the carrier concentration increases due to antistructural defects formed by the easy evaporation of Te. But the concentration balances by Te doping:

$$\mathrm{Tei}^x + \mathrm{VBi}^x \rightarrow \mathrm{TeBi} + \mathrm{e}'$$

where VBi^x is Bi vacancy and e' is electron produced. The newly formed electron compensates the excess Hall concentration of p-type Sb_2Te_3–25% Bi_2Te_3 thermoelectric materials, resulting in increasing Seebeck coefficient. The relationship can be explained by an equation as $\alpha = \gamma\text{-}\ln n$ at a certain temperature, where γ is scattering factor and n is carrier concentration [8].

Improvement of α by annealing treatment may correspond to the activated Te re-diffusion into the matrix with the microstructural homogenization effect [9]. In addition, the use of fine powder lowers the n and enhances γ in accordance with the easy Te diffusion and increase of the number of grains, resulting in the increase of α. The highest value of α was obtained from the specimens sintered with the fine powders at 450 °C, where the maximum R_H value was shown. The effect of annealing on the R_H as well as Hall conductivity will be discussed later.

Electric conductivity (σ) was increased from 718 $\Omega^{-1}\,cm^{-1}$ to 793 $\Omega^{-1}\,cm^{-1}$ for the fine powder and 769 $\Omega^{-1}\,cm^{-1}$ to 821 $\Omega^{-1}\,cm^{-1}$ for the coarse powder with increasing the sintering temperature from 400 °C to 450 °C, respectively, as shown in Fig. 4. However, it was decreased drastically to 503 $\Omega^{-1}\,cm^{-1}$ and 665 $\Omega^{-1}\,cm^{-1}$, respectively, by increasing the sintering temperature to 500 °C. The sudden decrease might be due to the low density and the high vacancy content of the sintered body, whereas the maximum value at 450 °C is due to increase of the density. In addition, the reaction rate for the vacancy formation would be activated for the fine powder due to higher surface area, resulting in the lowered σ. Unlike the Seebeck coefficient, the highest conductivity was obtained for the coarse powder. This opposite behavior corresponds to a relationship between the electric conductivity (σ) and carrier concentration (n) as well as the carrier mobility (μ) described as $\sigma = ne\mu$.

The thermal conductivity (K) became low by annealing and increasing the sintering temperature from 450 °C to 500 °C, but remained almost constant between 400 °C and 450 °C (not shown here). In order to know the effect of annealing on the electric and thermal conductivities, the Hall coefficient and mobility of sintered material were measured as shown in Table 2. Here, the sample sintered at 450 °C was used, because it recorded the maximal value. Annealing the specimen at 380 °C caused an increase of the Hall coefficients in both fine (33–90 μm) and coarse (91–355 μm) powders from $4.301 \times 10^{-7}\,m^3\,C^{-1}$ to $4.89 \times 10^{-7}\,m^3\,C^{-1}$ (about 14.7% improvement) and from $4.19 \times 10^{-7}\,m^3\,C^{-1}$ to $4.75 \times 10^{-7}\,m^3\,C^{-1}$ (about 13.4% improvement) respectively. However, the increase in the Hall mobility is only about 1.26% for the fine and 1.34% for the coarse powders. Thus, we can say that the annealing treatment is useful for controlling the Hall concentration by Te re-diffusion and homogenization, and not for the Hall mobility.

Fig. 5 shows a thermoelectric figure of merit (Z) driven by a combination of thermoelectric data presented above as a function of sintering temperatures, powder size and annealing treatment. The highest Z value of $2.788 \times 10^{-3}\,K^{-1}$ was obtained at 450 °C in the annealed fine powder. This result may correspond to the balance in carrier concentration and mobility due to the re-diffusion of Te during the annealing. In summary, the gas

Table 2
Annealing effect of p-type Sb_2Te_3–25% Bi_2Te_3 sintered body doped with 4 wt.% Te on Hall coefficient and mobility

Powder size	Hall coefficient ($\times 10^{-7}$ m^3 C^{-1})		Hall mobility ($\times 10^{-2}$ m^2 V^{-1} s^{-1})	
	As sintered	Annealed at 380 °C	As sintered	Annealed at 380 °C
90 μm	4.30	4.89	3.42	3.47
91–355 μm	4.19	4.75	3.44	3.49

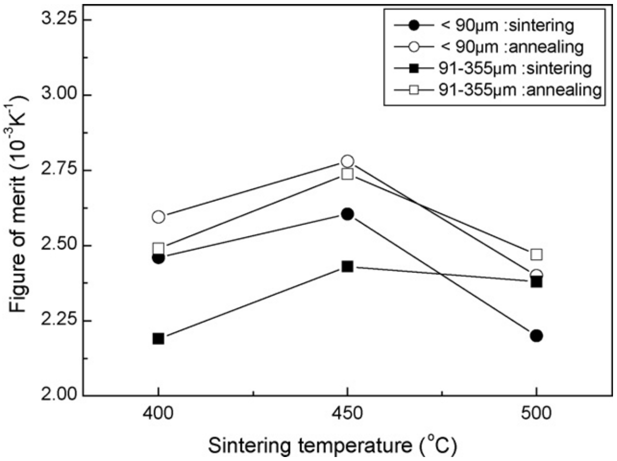

Fig. 5. Thermoelectric figure of merit (Z) plotted against the sintering temperatures, powder size and annealing.

atomization process would be an alternative way of fabricating the p-type thermoelectric compounds for mass productivity as well as the thermoelectric performance.

4. Conclusion

The as atomized p-type Sb_2Te_3–25% Bi_2Te_3 powders doped with 4 wt.% Te consisted of homogeneous Bi_2Te_3–Bi_2Sb_3 phases and presented a good density of 6.562 g/cm^3 by sintering at 450 °C under vacuum, with 97.5% of the theoretical density. Bending test strength of gas atomized alloy became about two times higher than alloy prepared by conventional casting process. The Seebeck coefficient was increased by annealing the fine powders, whereas the electric and thermal conductivities were increased using the coarse powders. Both mechanical and thermoelectric properties were maximized by sintering at 450 °C corresponding to the highest density. The Z value maximum was 2.788×10^{-3} K^{-1} after annealing the finer powders.

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