Thermoelectric Properties of Texture-Controlled $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Te}_{2.7}\text{Se}_{0.3}$ Compounds Prepared by Angular Extrusion Technique

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N-type $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Te}_{2.7}\text{Se}_{0.3}$ compounds were prepared by an angular extrusion technique with rapidly solidified and stacked foils. The extrusion temperature was varied from 653 to 838 K. Thermoelectric properties and the crystal orientation of the compounds were evaluated. The textures of the angular-extruded specimens were observed by Orientation Imaging Microscopy (OIM). The sizes of grains ranged from 4.6 to 16.2 μm in the specimens. The texture in the angular-extruded specimen showed that the basal plane was preferably aligned along the extrusion direction. Strong texture was observed in the specimens extruded at the temperature of 813 K. Electrical resistivity was shown to decrease with an increase in the angular-extrusion temperature. However the dependence of the carrier concentration on the extrusion temperature was small. Our study has shown that the decrease in electrical resistivity is mainly due to the increase of carrier mobility and that the carrier mobility strongly depends on the strength of the texture formed by angular extrusion. The highest Z value of $3.09 \times 10^{-3} \text{ K}^{-1}$ was derived from the specimen angular-extruded at 813 K. The present result indicates that the angular extrusion technique is effective in improving thermoelectric properties of bismuth-telluride based compounds. [doi:10.2320/matertrans.47.1941]

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1. Introduction

Bismuth-telluride based compound Bi_2Te_3 is a well-known thermoelectric material. This compound is generally utilized in thermoelectric cooling devices for precisely regulating the temperature of lasers used in telecommunications and for cooling high-wattage electronic devices such as microprocessors or biomedical components. Use of thermoelectric generating devices has lately become the focus of much attention.

The crystal structure of the Bi_2Te_3 compound is a rhombohedral structure of the space group $R\bar{3}m$.¹⁾ The electrical resistivity of the compound is known for its anisotropic properties due to the crystal structure. The compound is also known to easily fracture between the basal planes.

The figure of merit (Z) in eq. (1) denotes the performance index of thermoelectric materials:

$$Z = S^2 / (\rho \cdot \kappa) \quad (1)$$

where S is the Seebeck coefficient, ρ is electrical resistivity, and κ is thermal conductivity. Increasing the S or decreasing the ρ or κ is an effective method for producing thermoelectric materials with high Z value. Forming a fine orientated texture is especially effective in decreasing both the ρ and κ . Recently, plastic deformation techniques such as hot-extrusion and hot-forging on bismuth-telluride based compounds are also being intensively studied.²⁻⁵⁾ ECAE (Equal Channel Angular Extrusion) is a promising new technique for severe plastic deformation.^{6,7)} Applying ECAE and similar processes to bismuth-telluride based compounds has also been the subject of much research. These methods have proven effective in fabricating materials possessing excellent thermoelectric characteristics.^{8,9)} We also reported that applying angular extrusion technique with rapidly solidified and stacked foils of $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Te}_{2.7}\text{Se}_{0.3}$ is effective in improving thermoelectric properties of bismuth-telluride based compounds.¹⁰⁾ The angular extrusion technique is a technique

similar to ECAE but does not involve the "Equal Channel". The shape of the angular extrusion die inlet is not the same as the die outlet. The object of this paper is to study effects of the texture on thermoelectric properties of angular-extruded bismuth-telluride based compounds.

2. Experimental Procedure

We prepared alloy ingots of $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Te}_{2.7}\text{Se}_{0.3}$ by melting a mixture of elements ($\geq 99.99\%$) in a sealed evacuated silica tube. Using these alloy ingots, rapidly solidified foils were prepared by the single-roller melt-spinning technique in argon atmosphere. These foils were then sieved into a foil size of less than 1 mm. These sieved foils were stacked into an angular extrusion die of SKD61 tool steel. The shape of the die inlet is a circle 30 mm in diameter and the outlet is a rectangle of 30×6 mm. Angular extrusion was carried out in argon atmosphere at within a temperature range from 653 to 838 K. The crosshead speed was a constant 0.3 mm per minute. Angular-extruded specimens were cut into a size of $20 \times 30 \times 6$ mm. These were hot-pressed under a pressure of 100 MPa at 653 K in argon atmosphere in order to increase their density. Hot-pressing the rapidly solidified foil of bismuth telluride based compounds promotes grain growth at temperatures above 673 K.¹¹⁾ To prevent grain growth from hot-pressing after angular extrusion, the hot-pressing was performed at 653 K which is the lowest possible angular extrusion temperature. Figure 1 shows a schematic diagram describing angular extrusion and hot pressing processes. The thermoelectric properties S , ρ and κ were measured at room temperature in a direction parallel to the extrusion. The S and ρ specimens were rectangles of $0.90 \times 0.90 \times 2.46$ mm, and the κ specimen is a rectangle of $5 \times 5 \times 5$ mm. The κ value was measured using the static comparative method with a transparent SiO_2 cubic block as a reference sample. Electrical transport measurements by the Hall effect were made under a magnetic field of 0.5 T using ResiTest 8300 by Toyo

Fig. 1 Schematic diagram of angular extrusion.

Technica. Orientation Imaging Microscopy (OIM) measurements were made using a JEOL JSM5610 SEM equipped with a TSL EBSD system running OIM version 3. Calculations for grain sizes and textures were made based on OIM measurements for an area approximately $250 \times 200 \mu\text{m}$ using a hexagonal step size of $0.5 \mu\text{m}$. The datasets were cleaned and measurement points with Confidence Index < 0.05 were excluded.

3. Results and Discussions

3.1 Thermoelectric properties

Table 1 shows the thermoelectric properties S , ρ , κ , Power Factor (PF), and Z at various angular extrusion temperatures. Relative densities of the hot-pressed specimens angular extruded at 653, 733, 813 and 838 K were respectively, 98.2, 99.3, 99.8, 99.9 and 99.9%. A theoretical density 7.78 g/cm^3 was used here.¹²⁾ As can be seen in Table 1, there is little change in the S and κ . The ρ value gradually decreases below an extrusion temperature of 813 K, while it rises at an extrusion temperature of 838 K. The highest Z value of $3.09 \times 10^{-3} \text{ K}^{-1}$ was obtained for an angular-extruded specimen at an extrusion temperature of 813 K. The Z value is higher than that of typical hot-extruded n-type bismuth telluride based compounds which were reported as $2.6 \times 10^{-3} \text{ K}^{-1}$.^{2,3)}

Carrier mobility (μ) and carrier concentration (n) up to the extrusion temperature are plotted in Fig. 2. Here, ρ can be found from the following eq. (2):

$$\rho = 1/(n \cdot \mu \cdot e) \quad (2)$$

where e is the electron charge. As shown in Fig. 2, μ gradually increases below an extrusion temperature of 813 K, and starts to drop at an extrusion temperature of 838 K. The changes in S and n on the other hand were small. This

Fig. 2 Extrusion temperature dependence of carrier mobility (μ) and carrier concentration (n).

indicates that ρ is strongly dependent on μ .

It therefore becomes apparent that the μ depends on the extrusion temperature. The PF can therefore most likely be improved by controlling the angular extrusion temperature to increase the μ .

3.2 Texture formed by Angular Extrusion technique

Figure 3 shows inverse pole figure maps of specimen cross sections in the extrusion direction, and (001), (100) pole figures of specimens at each extrusion temperature. The pole marked "TD" is normal for the extrusion direction and "RD" is normal for the applied pressure direction in these pole figures. As seen in Fig. 3, all textures show the [001] direction of the specimen is preferably aligned across the extrusion direction. Average grain sizes of specimens angular-extruded at 653, 733, 813 and 838 K were respectively 4.6, 5.5, 11.0 and $16.2 \mu\text{m}$. The grain size increases along with a rise in the extrusion temperature. At a temperature of 813 K, the grain shape is obviously an ellipse and the longitudes of grains are along the extrusion direction. On the other hand, grains for specimens extruded at a temperature of 838 K undesirably develop isotropically. The current results reveal little change in the κ value even though the average grain size increases as the angular extrusion temperature rises. So, grain size has no effect on κ at these grain sizes. Figure 4 shows cumulative ratio of surface area of distribution angles for specimens angular-extruded at each temperature. Here, the angle between extrusion direction and the [001] direction of the point measured by EBSD is defined as the distribution angle (θ). Below 813 K, θ concentrates to

Table 1 Thermoelectric properties of angular-extruded specimens.

Extrusion Temperature T/K	S $/\mu\text{VK}^{-1}$	ρ $/\times 10^{-5} \Omega\text{m}$	κ $/\text{Wm}^{-1} \text{K}^{-1}$	PF $/\times 10^{-3} \text{Wm}^{-1} \text{K}^{-2}$	Z $/\times 10^{-3} \text{K}^{-1}$
838	-199.8	1.099	1.28	3.63	2.84
813	-199.6	0.990	1.30	4.02	3.09
733	-198.9	1.056	1.32	3.75	2.84
693	-199.6	1.078	1.32	3.70	2.79
653	-199.3	1.155	1.30	3.44	2.65

Fig. 3 Inverse pole figure maps and (001), (100) pole figures of angular-extruded specimens extruded at (a) 653 K, (b) 733 K, (c) 813 K and (d) 838 K.

Fig. 4 Angle (θ) distribution at extrusion temperature.

90 degrees along with a rise in extrusion temperature, while the angle disperses slightly at an extrusion temperature of 838 K. The result reveals that grains develop along with formation of the texture by angular extrusion at temperatures below 813 K. This result also shows that grain growth without formation of the texture is predominant over formation of the texture by angular extrusion at an extrusion temperature of 838 K. This demonstrates that isotropic grain growth lowers the μ . Figure 5 shows the relation between μ and the preferred orientation angles (P) of the angular-extruded specimens. Here, P is defined as the value obtained from subtracting the distribution angle (θ) from 90 degrees when the ratio of surface area is equal to 0.2. Figure 4 for

example shows the P value at 813 K. The P value indicates the angle where basal planes disperse from the extrusion direction for 80 percent of the ratio of surface area. The P value therefore indicates the strength of the texture of the angular-extruded specimen. Figure 5 indicates that the carrier mobility is greatly dependent on the strength of the texture formed by angular extrusion technique. Moreover, there is little change in the S and κ versus changes in the texture strength and grain size. So, the figure of merit (Z) for bismuth-telluride based compounds can be improved by controlling the angular extrusion temperature to increase carrier mobility (μ).

4. Summary

N-type $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Te}_{2.7}\text{Se}_{0.3}$ compounds were prepared by the angular extrusion technique with rapidly solidified and stacked foils. Grains were obtained in sizes ranging from 4.6 to $16.2\mu\text{m}$. The texture in the angular-extruded specimen shows that the basal plane should preferably be aligned along the extrusion direction. Our study shows that carrier mobility (μ) depends on the strength of the texture. The resultant Z value reached a maximum of $3.09 \times 10^{-3} \text{ K}^{-1}$ for specimens that were angular-extruded at 813 K. Angular extrusion is therefore effective in controlling the texture of bismuth-telluride based compounds and improving their thermoelectric properties.

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Fig. 5 Relation between preferred orientation angle (P) and carrier mobility (μ).

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