Consolidation and Microstructure Control of Bismuth Antimony Telluride by Compressive Torsion Forming

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Bismuth antimony telluride has the best performance among the p-type thermoelectric materials used in the range of temperature between 300 K and 500 K. This material has a trigonal-hexagonal scalenohedral crystal structure and the cleavage parallel to the basal plane of the crystal can readily occur. Suppression of the electrical resistivity and the thermal conductivity will be effective for further improvement of the performance of the thermoelectric elements made from this material. The compressive torsion forming is the severe plastic deformation technique, in which the loads of compression and distortion are simultaneously subjected to the materials without change in its shape. In this work, we have applied this technique to the powder of bismuth antimony telluride for consolidation and improvement of the thermoelectric performance by refining the grain structure and by controlling the crystal orientation. The samples consolidated under various forming conditions were investigated with respect to density, microstructure, XRD, texture, and thermoelectric properties. It was found out that the compressive torsion forming is effective for the microstructure control, the grain structure less than 10 μm can be obtained, and the thermoelectric performance is obviously improved by the compressive torsion forming. [doi:10.2320/matertrans.MA200705]

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1. Introduction

Bismuth antimony telluride materials have been currently used for many thermoelectric products in temperature level of 300 K to 500 K due to their high performance. But lower cost of production and higher thermoelectric performance of the materials will be further required. In general, the thermoelectric performance is defined with a following equation.

\[ Z \equiv \frac{S^2}{\rho \cdot \kappa} , \]  

(1)

where \( Z \) is the thermoelectric figure of merit [K\(^{-1}\)], \( S \) the Seebeck coefficient [V/K], \( \rho \) the electrical resistivity [Ωm] and \( \kappa \) the thermal conductivity [Wm\(^{-1}\)K\(^{-1}\)], respectively. These three component properties are mainly influenced by carrier concentration and carrier mobility. Thus, the figure of merit \( Z \) essentially depends on the material except crystal with anisotropic structure.

The bismuth antimony telluride has a trigonal-hexagonal scalenohedral crystal structure of space group R-3m. The crystal is composed of stacked hexagonal layers that can be readily cleat in basal planes. In the layer of like atoms that follow the sequence of -Te-(Bi, Sb)-Te-(Bi, Sb)-Te-, the Te-(Bi, Sb) combinations are held by strong ionic-covalent bonds and the adjacent Te-Te combination is held by weak van der Waals bonding that accounts for the ease of cleavage.\(^{1)}\) The layer stacking brings to a highly anisotropic structure. In this crystal structure, the electrical resistivity \( \rho \) and the thermal conductivity \( \kappa \) in the direction parallel to the c-axis are four times greater and half times greater than those in the perpendicular direction, respectively.\(^{2,3)}\) Since the anisotropic behavior of electrical resistivity is greater than that of thermal conductivity, the maximum figure of merit is obtained in the perpendicular direction to the c-axis in the single crystal. The single crystal of bismuth antimony telluride, however, is not suitable to produce the thermoelectric element due to ease of cleavage in direction parallel to the basal plane.

Polycrystal bismuth antimony telluride is usually used for the thermoelectric element in order to improve the mechanical property. It is most important for the polycrystal bismuth antimony telluride to arrange the c-axis of the grain in one direction for using the anisotropic nature of the thermoelectric property. Grain refining also helps to improve the mechanical property, and to decrease the thermal conductivity by the phonon scattering. In recent years, the severe plastic deformation processes such as equal-channel angular processing\(^{4,5)}\) and accumulative roll-bonding\(^{6)}\) have been developed to obtain ultra-fine grains. We have developed a severe plastic deformation process named compressive torsion forming technique,\(^{7-10)}\) in which the loads of compression and distortion are simultaneously subjected to the materials without change in its shape. In this process, the grain refining and the control of crystal orientation can be expected. In this study, the compressive torsion forming was applied to the powder of bismuth antimony telluride for consolidation and improvement of the thermoelectric performance by refining the grain structure and by controlling the crystal orientation. The powder was consolidated under various forming conditions. Measurements of density, microstructure, X-ray diffraction (XRD), texture, and thermoelectric properties were carried out to the consolidated samples. Influences of the forming conditions on the micro-

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structure, crystal orientation, and thermoelectric properties were investigated.

2. Experimental

The powder (particle size range: 34–108 µm) was prepared by mechanical milling of the one-directionally solidified Bi$_{0.4}$Sb$_{1.6}$Te$_3$ rod. Figure 1 shows an optical micrograph of cross sections of the powder particles.

Compaction of the powder was carried out in a cylindrical die, and the compacted body of 25 mm in diameter and of about 10 mm in height was prepared as a starting sample for the compressive torsion forming. A schematic diagram of the compressive torsion forming is shown in Fig. 2. In this apparatus, the loads of compression and distortion are simultaneously subjected to the compacted powder without change in its shape at elevated temperature. In this work, we attempted two kinds of torsion loading in the forming. One is the repeat torsion loading, in which rotating direction of punch is reversed at a given twist angle. Another one is the one-directional torsion loading, in which rotating direction of punch is not changed. The fixed forming conditions were the forming temperature of 723 K, the compression pressure of 75 MPa and the rotational speed of 5 rpm. The twist angle and the twist cycle in the repeat torsion loading or the rotation cycle in the one-directional torsion loading were changed as the forming conditions as shown in Table 1. In three forming conditions of the repeat torsion loading, the total torsion angle of both the upper and lower punches was made constant with 7,200°/C14. For comparison, the samples were also consolidated by the ordinary compression forming under the same temperature and the same compression pressure.

The relative density was obtained as a ratio of the density to the theoretical density. Both ends of a specimen were soldered with pure copper electrodes for measurements of the thermoelectric properties. The Seebeck coefficient $S$ was obtained by measuring the electromotive force generated by giving temperature difference of 10 K to the both ends. The electric resistance $r$ [Ω] was measured with milliohmmeter. The electrical resistivity $\rho$ was calculated from an equation $\rho = ra/l$, where $a$ and $l$ are the sectional area [m$^2$] and the length [m] of the specimen, respectively. The thermal conductivity $\kappa$ was measured based on the Harman method.$^{11}$ All of the thermoelectric properties were measured at 300 K in the direction perpendicular to the compression direction, that is, in the radial direction of the consolidated sample. The measurements of XRD and texture were carried out on the cross-section that is perpendicular to the direction of compression. Influences of the forming conditions on the microstructure, crystal orientation, and thermoelectric properties were investigated.

3. Results and Discussion

The relative densities of the samples consolidated under
various forming conditions are listed in Table 1. All samples had good relative density of more than 96% as well as the ordinary compression forming (Sample No. 1). This fact indicates that the bismuth antimony telluride can be sufficiently consolidated by this forming method.

Figure 3 shows the microstructure of the sample consolidated by the ordinary compression forming. The relatively slender shape (platy shape in three dimension) grains of several ten micrometers in thickness are arranged in the direction perpendicular to compression. The grains inherit the morphology of the milled powder particles as shown in Fig. 1. The microstructure of outer part (Part-A in Fig. 4(a)) in the cylindrical sample (Sample No. 2) consolidated by the compressive torsion forming is shown in Fig. 4(b). Even by adding torsion loading with small torsion angle or small number of torsion cycle, the grains in the Part-A were refined into several micrometers. In the part near the center axis or near the middle height of the sample like as Part-B in Fig. 4(a), however, it was not easy to progress the grain refining because of small share deformation in the part. This is originated from the geometric characteristic of the torsion loading. Figure 5 shows the microstructures of the central part like as the Part-B in Fig. 4(a) of the samples consolidated under various forming conditions. Figure 5(a) and (b) are the microstructures of the samples consolidated by using one-directional torsion loading, respectively. Though the grain refining in the central part of the sample did not progress by subjecting the repeat torsion loading with small twist angle to the sample, it progressed by subjecting the repeat torsion loading with large twist angle or the one-directional torsion loading to the sample. The grain size of less than 10 µm could be obtained in not only peripheral part but also central part.

As an index to quantitatively evaluate the orientation frequency of basal plane in the hexagonal system, the ratio of intensity \( RI \) is defined as follows.

\[
RI = \frac{I_{006} + I_{0015}}{I_{006} + I_{0015}}
\]

where \( I_{hkl} \) is the measured X-ray intensity of (hkl) plane and \( I_{006} \) and \( I_{0015} \) are the random X-ray intensity of (006) and (0015) planes, respectively. The (006) plane has the strongest value in the random X-ray intensity of the bismuth antimony telluride. The ratio of intensity \( RI \) has a value of more than unity. The larger the ratio of intensity \( RI \) is, the more basal planes on the traverse cross section of the sample exist. The results of \( RI \) of the samples consolidated under various forming conditions are listed in Table 1. The \( RI \) value greatly improved by the compressive torsion forming. Especially, the \( RI \) value of the sample (Sample No. 2) was remarkably large. In this condition, the grain refining was insufficient as shown in Fig. 5(a). On the other hand, the \( RI \) value of the sample in which the grain refining sufficiently progressed has not improved so much.

Examples of the measurement results in the texture are shown in Fig. 6. Figure 6(a) shows the (006) pole figure in the traverse cross section of the cylindrical sample (Sample No. 2). It indicates that the basal plane (c-plane) is parallel to the traverse cross section of the sample. It was found out that the basal plane (Sample No. 6) was slightly inclined to the traverse cross section of the sample shown in Fig. 6(b). This fact corresponds to the \( RI \) value not being remarkably large.

The thermoelectric properties were measured at five different radial positions in a sample. In all samples, the changes of the properties in the different positions were relatively small, and there were not the systematical position dependences on the properties. Thus, the properties were

Fig. 3  Microstructure of sample consolidated by compression forming.

Fig. 4  (a) Observation parts of microstructure and (b) microstructure of Part-A in sample consolidated by compressive torsion forming.
evaluated as an average value in the five specimens of a sample. The relation between the ratio of intensity $RI$ and the Seebeck coefficient $S$ is shown in Fig. 7. There was not a clear relation between them. Though the Seebeck coefficient $S$ in the compression forming (Sample No. 1) was about 4% lower than average value in five kinds of the compressive torsion forming (Sample Nos. 2–6), the different forming conditions did not lead to large difference in the values.

Figure 8 shows the relation between the ratio of intensity $RI$ and the electrical resistivity $\rho$. The electrical resistivity $\rho$ in the compression forming was relatively higher than those in the compressive torsion forming. The low degree of crystal orientation in the compression forming might cause high electrical resistivity. The increase in the crystal orientation would contribute to the decrease in the electrical resistivity regardless of the progress of grain refining.

Figure 9 shows the changes in the thermal conductivity with the crystal orientation. The thermal conductivity $\kappa$ in the compression forming was lower than those in the compressive torsion forming. The tendency of the change was reverse to that of electrical resistivity. Generally, the thermal conductivity $\kappa$ of thermoelectric semiconductors consists of contributions from electrons and phonons, with the majority contribution coming from phonons. It is expressed with the following equation.

$$\kappa = \kappa_E + \kappa_L,$$

where $\kappa_E$ and $\kappa_L$ are the electron and lattice thermal conductivities, respectively. According to the Wiedemann-Franz law, the electron thermal conductivity $\kappa_E$ is calculated as follows.

$$\kappa_E = \frac{LT}{\rho},$$

where $L$ and $T$ are the Lorenz number $[V^2K^{-2}]$ and the absolute temperature $[K]$, respectively. When the electron thermal conductivity is ruled by the lattice scattering of carrier, the Lorenz number is expressed as follows.

$$L = 2\left(\frac{k_B}{e}\right)^2 = 1.485 \times 10^{-8},$$

where $k_B$ and $e$ are Boltzmann constant $[JK^{-1}]$ and elementary electric charge $[C]$, respectively. The lattice thermal conductivity $\kappa_L$ is fundamentally independent of the electron thermal conductivity $\kappa_E$. Figure 10 shows the relation between the electron and the lattice thermal conductivities calculated with eqs. (3) and (4). There was a tendency that the lattice thermal conductivity increases with the electron thermal conductivity. Though this is a characteristic result, the further investigation about the thermal...
conductivity, the grain refining, and the crystal orientation will be required for the exact explanation of this result.

Figure 11 shows the relation between the ratio of intensity $RI$ and the figure of merit $Z$ calculated with eq. (1). There was not a clear relation between them. This will be mainly caused by the unclear relation between the crystal orientation and the Seebeck coefficient. But the thermoelectric performance was obviously improved by the compressive torsion forming that contributes to both the crystal orientation and the grain refining.

4. Conclusions

The bismuth antimony telluride powder was consolidated by the compressive torsion forming. The density, microstructure, crystal orientation, and thermoelectric properties were investigated. The results are summarized as follows;

(1) The bismuth antimony telluride powder can be sufficiently consolidated by the compressive torsion forming.

(2) Though the grain refining in the central part of the sample did not progress by subjecting the repeat torsion loading with small twist angle to the sample, it progressed by subjecting the repeat torsion loading
with large twist angle or the one-directional torsion loading to the sample.

(3) The orientation of basal planes in the hexagonal crystal was improved greatly by the compressive torsion forming, and the improvement of crystal orientation was especially remarkable in subjecting the repeat torsion loading with twist angle of 45°/C14° in 40 cycles to the sample.

(4) Though the compressive torsion forming improved the Seebeck coefficient, there was not a clear relation between the crystal orientation and the Seebeck coefficient.

(5) The electrical resistivity was decreased with improvement of the crystal orientation.

(6) Improvement of the crystal orientation by the compressive torsion forming mainly contributed to increase in thermal conductivity, and the lattice thermal conductivity increased with the electron thermal conductivity.

(7) The thermoelectric performance was obviously improved by the compressive torsion forming.

REFERENCES