Microstructure and Thermoelectric Properties of Hot-Pressed n-Type Bi₁₋₀.₉Sb₀.₁Te₂₋₀.₆Se₀.₄ Alloys Prepared Using a Rapid Solidification Technique

Yuma Horio, Hiroyuki Yamashita and Takahiro Hayashi

Material & Components Development Center, YAMAHA Corporation, Iwata-gun 438-0192, Japan

N-type Bi₁₋₀.₉Sb₀.₁Te₂₋₀.₆Se₀.₄ alloys were prepared by a rapid solidification technique and subsequent hot-pressing method. The microstructure and thermoelectric properties of the alloys were investigated as a function of the hot-pressing temperature and pressure. The X-ray diffraction measurements indicate that the grains are preferably aligned with the c-axis perpendicular to the direction of the hot-pressing force by the hot-pressing. Hot-pressing at higher temperatures promotes the grain growth in the alloys. The Seebeck coefficient (S) and electrical resistivity (ρ) decrease with an increase in the hot-pressing temperature, whereas the thermal conductivity (κ) increases. The specimens prepared under a higher temperature greater than 733 K show better thermoelectric performance: the largest dimensionless figure of merit (ZT) is 1.08 at room temperature.

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1. Introduction

Controlling the crystal orientation and grain size is well known to be practically effective for optimizing the thermoelectric properties of bismuth-telluride based alloys. Bi₂Te₃ crystallizes in a rhombohedral structure with a space group D₃d (R̅3m) and with five atoms in a trigonal cell. The structure can be represented as a stack of hexagonally arrayed atomic planes; each consisting of only one type of atom. The electrical resistivity (ρ) of this alloy is known to be anisotropic. The ρ is higher along the c-axis than in the basal plane due to the Te-Te double layer being parallel to the basal plane (c-plane). The crystal is therefore easily cleaved at this layer in the hexagonal unit cell, due to the weakness of the van der Waals type bond between the layers.

Powder metallurgy techniques such as the hot-pressing method with a pulverized ingot have been widely employed to improve thermoelectric properties of the product. They have an advantage of producing a homogeneous material with reduced thermal conductivity (κ). However, the crystal orientation may potentially be lost during the pulverizing process, resulting in an increase in ρ. We proposed a new rapid solidification process for fabricating new bismuth-tellurides for thermoelectric use. The rapid solidification technique can be expected to make ρ lower in the direction parallel to the foil thickness rather than other directions. We previously reported that, in rapidly solidified foils fabricated using the single roller method, grains are formed with the c-plane perpendicular to the surface of the cooling roller during the solidification process. Furthermore, the formation of fine crystal grains in the alloy foil will also be effective in obtaining a low κ value.

The purpose of this work is to investigate the effects of hot-pressing conditions on the microstructure and thermoelectric properties of the n-type Bi₁₋₀.₉Sb₀.₁Te₂₋₀.₆Se₀.₄ alloy prepared using rapidly solidified foil. We also report on variations of the microstructure, including the crystal orientation, with the hot-pressing temperature and pressure.

2. Experimental Procedure

The Bi₁₋₀.₉Sb₀.₁Te₂₋₀.₆Se₀.₄ alloy ingots were prepared by melting a mixture of pure Bi, Sb, Te and Se (≥99.99% purity). The raw materials were sealed into a fused silica tube with argon gas filled. Then, the raw materials were melted at 923 K for 1 h using a rocking furnace. The single roller melt spinning technique was then employed to obtain rapidly solidified foils. The copper roller with 400 mm diameter was rotated at a speed of 10.5 s⁻¹. The obtained foils were 2.0 mm in width and 10 to 20 μm in thickness. They were annealed in a Pyrex tube with hydrogen gas for 10 h at 653 K as part of the reduction process.

The foils were then carefully stacked in a die in order to maintain an effective crystal orientation. Careful handling of the foils was essential at this point since the foils were very brittle along their cleavage plane in the hexagonal unit cell and easily pulverized. The stacked foils were then hot-pressed in a direction parallel to the foil thickness. Two pellets with thickness of 8 mm were formed to have diameters of 10 and 26 mm, respectively. The two pressures, 10 and 50 MPa, were employed to examine the effect of hot pressing on the microstructure and thermoelectric properties of the pellets. We also expected optimization of the pressures to consolidate the foils without breaking them.

Two types of specimens (A) and (B) were fabricated. The specimens (A) were obtained by hot-pressing in the temperature range between 553 and 763 K in an argon atmosphere for 60 min at 10 and 50 MPa. The specimens (B) were fabricated by a two-step hot-pressing process. The foils were hot-pressed at 50 MPa for 60 min at temperatures ranging from 553 to 703 K in the initial hot-pressing step and subsequently hot-pressed at 30 MPa for 30 min at a temperature of 733 K in the second step. Hot-pressing conditions such as the pressure, temperature and time of the hot pressing were carefully chosen to control the grain size and crystal orientation of the specimens.

The X-ray diffraction measurements were performed on the plane perpendicular to the pressing direction for all the hot-pressed specimens to examine the orientation of the
grains. The microstructure of the specimens was observed by optical micrograph.

The thermoelectric properties were measured at room temperature in a direction parallel to the pressing direction. To measure the Seebeck coefficient ($\alpha$) and $\kappa$ of the alloy, specimens with dimensions of $4 \times 4 \times 4$ mm were cut out from the hot-pressed ingots. The thermoelectric motive force ($E$) was also measured under the application of a small temperature differential ($\Delta T$) between both ends of the specimen. The $\alpha$ value was determined from the formula $E/\Delta T$. The $\kappa$ value was measured using the static comparative method, with a transparent SiO$_2$/C$_0$ cubic block as a standard sample in a vacuum of $5 \times 10^{-3}$ Pa. The $\rho$ value was measured using the four-probe technique. The figure of merit ($Z$) was evaluated by the relation of $Z = \alpha^2/(\rho \cdot \kappa)$.

3. Results and Discussion

3.1 X-ray diffraction

Figure 1 shows the X-ray diffraction of a specimen (A) hot-pressed at 50 MPa for 60 min at 553 K and a specimen (B) subsequently hot-pressed at 30 MPa for 30 min at 733 K for the specimen (A) in the second step. The X-ray diffraction intensities of basal planes such as (0015) and (0018) planes were weak in comparison with those of (110) and (1010) planes for both specimens (A) and (B). This finding indicates that the grains are preferably aligned with their c-axis perpendicular to the direction of the hot-pressing force by the hot-pressing. It is also concluded that the difference in the crystal orientation is small between the two specimens, even though the intensity of the (110) plane is reduced by the second pressing for the specimen (B).

Figure 2 shows the diffraction intensity ratio ($R$) of specimens (A) and (B) as a function of the hot-pressing temperature in the first step. Here, “$R$” has been determined using the following equation, $R = I(h, k, l)/\Sigma I(h, k, l)$, where “$I$” is the X-ray diffraction intensity and $\Sigma I(h, k, l) = I(101) + I(015) + I(018) + I(1010) + I(110) + I(0015) + I(205) + I(0018) + I(0210)$. Higher $R$ values are found at temperatures lower than 583 K for both specimens (A) and (B), suggesting that the hot-pressing temperature in the first step determines the orientation of the grains. The grain growth in the specimens (A) and (B) will be demonstrated in the optical micrographs.

3.2 Microstructure

Optical micrographs are shown in Fig. 3 for Bi$_{1.9}$Sb$_{0.1}$Te$_{2.6}$Se$_{0.4}$ alloy specimens (A) hot-pressed at 50 MPa for 60 min at (a) 553 K and at (b) 763 K. Figure 4 also shows the optical micrographs of specimens (A) hot-pressed at 10 MPa for 60 min at (c) 673 K and at (d) 763 K. Grain growth is found for the specimens hot-pressed at the higher temperature of 763 K irrespective of any difference in hot-pressing pressure. This is a strong evidence to show that the hot-pressing at higher temperature promotes grain growth in the specimen (A).

Figure 5 shows the optical micrographs of the specimens (B) hot-pressed at (e) 553 K and (f) 703 K in the first hot-pressing step. It is found that the crystal grain size in (e) is still as small as those in (a) and (c). However, in (f), an appreciable grain growth is observed. Keeping in mind that the specimens (B) are fabricated by a further hot-pressing process at a temperature of 733 K and for a shorter time (30 min), it is concluded that hot-pressing at higher temperature (at higher than 700 K) promotes grain growth more.

3.3 Thermoelectric properties

Figure 6 illustrates the variation of the $\alpha$, $\rho$, $\kappa$ and figure of merit ($Z$) values of hot-pressed Bi$_{1.9}$Sb$_{0.1}$Te$_{2.6}$Se$_{0.4}$ specimens (A) and (B) as a function of the hot-pressing temperature in the first step.

The $\alpha$ value decreases with the increase in the hot-pressing temperature to 673 K for the specimens (A) hot-pressed at 50 MPa and specimens (B). The relative variations of the decrease in $\alpha$ values are 13% for both specimens. The same temperature dependence of $\alpha$ is observed in specimens (A) hot-pressed at 10 MPa. Specimens that were hot-pressed at
Fig. 3 Optical micrographs of Bi$_{1.9}$Sb$_{0.1}$Te$_{2.6}$Se$_{0.4}$ specimens (A) hot-pressed at (a) 553 K and (b) 763 K. (50 MPa, 60 min)

Fig. 4 Optical micrographs of Bi$_{1.9}$Sb$_{0.1}$Te$_{2.6}$Se$_{0.4}$ specimens (A) hot-pressed at (c) 673 K and (d) 763 K. (10 MPa, 60 min)

Fig. 5 Optical micrographs of Bi$_{1.9}$Sb$_{0.1}$Te$_{2.6}$Se$_{0.4}$ specimens (B) hot-pressed at (e) 553 K and (f) 703 K in first step. (50 MPa, 60 min)
temperatures of 613 K or higher, however, show small variation in $\alpha$. There is no significant difference in the temperature dependence of $\alpha$ for the specimens (A) hot-pressed at 10 and 50 MPa and the specimens (B); despite the fact that the hot-pressing temperature in the first step is lower than that in the second step for specimens (B).

The $\rho$ value decreases by 65% with the increase in the hot-pressing temperature for the specimens (A) hot-pressed at 10 and 50 MPa. The change in $\rho$ is large at temperatures ranging from 553 to 613 K for specimens hot-pressed at 50 MPa. For the specimens (B), the $\rho$ value gradually decreases as the hot-pressing temperature increases. The variation in $\rho$ for the specimens (B) is 12%, which is smaller than that for the specimens (A).

The $\kappa$ value increases by 13% as the hot-pressing temperature rises in specimens (A) hot-pressed at 10 and 50 MPa. For the specimens (B), the $\kappa$ value is gradually increased by 4% as the hot-pressing temperature rises.

The figure of merit ($Z$) decreases by 18% as the hot-pressing temperature rises in the specimens (B). The $Z$ values for the specimens (B) are higher than those for the specimens (A) hot-pressed at 10 and 50 MPa. However, the $Z$ shows high values at higher temperatures than 733 K in the specimens (A).

Variation in $\alpha$, depending on the carrier concentration, has been reported previously. The carrier concentration in n-type thermoelectric materials is generally known to increase in correlation with the increase in the number of electrons. The increase in the carrier concentration has the effect of lowering $\alpha$. In this study, an increase in hot-pressing temperature causes both $\alpha$ and $\rho$ to decrease, thus showing the close relationship between $\alpha$ and $\rho$.

The $\kappa$ value is also closely related to carrier concentration and phonon scattering at grain boundaries because it can be expressed as $\kappa = k_{el} + k_{ph}$. Here, $k_{el}$ is the electron contribution to thermal conductivity and $k_{ph}$ is the lattice thermal conductivity. The grain growth, as shown in Figs. 3 and 4, contributes to the increase of $\kappa$ with a higher $k_{ph}$ due to phonon scattering. Assuming the Wiedemann–Franz’s law, for the specimen (A) hot-pressed at 50 MPa for 60 min at 763 K, the $k_{el}$ and $k_{ph}$ are calculated to be 0.33 and 0.92 W·m$^{-1}$·K$^{-1}$ respectively. It is indicated that $k_{ph}$ contributes to the total value of $\kappa$.

For the specimens (A) hot-pressed at 10 MPa, $\rho$ is found to have a low value of $1.02 \times 10^{-5}$ Ω·m with the increase in the hot-pressing temperature. As shown in Fig. 6, the specimens (A) exhibit a figure of merit ($Z$) of $3.43 \times 10^{-3}$ K$^{-1}$ due to the low value of $\rho$. It is found that a higher $Z$ value than $3.40 \times 10^{-3}$ K$^{-1}$ is obtained through optimization of the hot-pressing temperature in the one-step hot-pressing process for Bi$_{1.0}$Sb$_{0.1}$Te$_{2.0}$Se$_{0.4}$ specimens using rapidly solidified foils.

For the specimens (B), the $\kappa$ values are as small as 1.0 W·m$^{-1}$·K$^{-1}$; representing a high figure of merit ($Z$) of above $3.10 \times 10^{-3}$ K$^{-1}$ when the specimens (B) is hot-pressed at hot-pressing temperatures below 613 K. The $\kappa$ values obtained are lower than those reported for alloys prepared using conventional techniques. A maximum figure of merit ($Z$) of $3.61 \times 10^{-3}$ K$^{-1}$ is obtained for the specimen hot-pressed at 553 K. This high $Z$ value was obtained with high $\alpha$ and $\kappa$ respectively, even though this specimen also exhibits a high $\rho$ of $1.46 \times 10^{-5}$ Ω·m. Therefore, a dimensionless figure of merit ($ZT$) of 1.08 is obtained. The value is higher than previously reported for hot-extruded or hot-pressed alloys. At hot-pressing temperatures exceeding 643 K, the $Z$ value was seen to increase with an increase in hot-pressing temperature for the specimens (B). The resulting $Z$ value of $3.22 \times 10^{-3}$ K$^{-1}$ prepared at a temperature of 703 K, is due to lower $\rho$. It is thus concluded that an essential factor in obtaining a high $Z$ value involves fabricating the specimens with a high $\alpha$ and low $\kappa$ by lowering the hot-pressing temperature, or the specimens with a low $\rho$ by raising the hot-pressing temperature.

Figure 7 shows the variation of $Z$ as a function of $R$ for the
specimens (A) and (B). It shows that $Z$ values increase with the increase of $R$, especially for specimens (B). We conclude that increasing of $R$ to a high value is a vital factor in obtaining a high value of $Z$ for specimens using rapidly solidified foils.

4. Summary

The $\alpha$, $\rho$, $\kappa$ and $Z$ values of hot-pressed specimens prepared using rapidly solidified Bi$_{1.9}$Sb$_{0.1}$Te$_{2.6}$Se$_{0.4}$ have been evaluated. Their microstructures are observed and the crystal orientations are also investigated.

(1) The X-ray diffraction measurements indicate that the grains are aligned with the $c$-axis perpendicular to the direction of the hot-pressing force by the hot-pressing process.

(2) The hot-pressing at higher temperature promotes the grain growth for specimens (A) and (B).

(3) For both the specimens (A) and (B), the decreasing of the hot-pressing temperature is effective way to obtain a high $Z$ value with high $\alpha$ and low $\kappa$. Whereas, the specimens with low $\rho$ shows a high $Z$ through the raising of the hot-pressing temperature. By considering that the specimens (B) was hot-pressed at 733 K, the raising of hot-pressing temperature is thought to be more effective to obtain a higher $Z$.

(4) There is a little difference in the pressing pressure dependence for the specimens (A) hot-pressed at 10 and 50 MPa.

The specimens (B) fabricated by the two-step hot-pressing process exhibits the highest dimensionless figure of merit ($ZT$) of 1.08.

REFERENCES