Microstructure and Thermoelectric Properties of Hot-Pressed p-Type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Alloys Prepared by Rapid Solidification Technique

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Rapidly solidified bismuth-telluride based alloy foil; fabricated using the single roller melt spinning method exhibits a fine microstructure with unidirectional crystals. Meanwhile, a hot-pressing process, using rapidly solidified foils, was used to prepare the consolidated samples. The fine microstructure of this alloy is extremely effective in decreasing thermal conductivity because of the grain boundary scattering of the phonons, a key factor improving the thermoelectric properties of thermoelectric materials. Hot-pressed samples using these rapidly solidified foils display lower thermal conductivity values than the alloys made by the conventional hot-consolidating method using pulverized ingot powder. In this case, thermoelectric properties were investigated comparatively in terms of hot-pressed rapidly solidified foil specimens and pulverized powders of these foils under 53 μm in size, evaluating the dependence of the hot-pressing temperature and consequent pressure on the thermoelectric properties of these specimens. The maximum figure of merit (Z) obtained was $3.34 \times 10^{-3} \text{ K}^{-1}$.

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1. Introduction

Recently several studies have outlined new means of fabricating high performance thermoelectric semiconductor materials, which can generally be categorized into two types. The first is prepared through unidirectional solidification techniques, such as the zone melting, Czochralski or Bridgman methods.¹⁻⁵⁾ However, such materials prepared possess poor mechanical properties since they are prone to fracture along the cleavage planes of their own crystalline structure. To eliminate this weakness, other types of materials have been studied and reported on in recent years, namely those prepared by sintering or hot-pressing a pulverized ingot into a solid form.⁶⁾ Despite considerable mechanical strength and low thermal conductivity, these hot-pressed materials have a lower figure of merit (Z) than unidirectional solidified materials. This is due to the low carrier mobility resulting in high electrical resistance. During pulverization, the powder surface can also be easily contaminated by oxygen or other impurities, compounding the lack of carrier mobility present in these hot-pressed materials made from such powders. The powder size and surface of these pulverized powders are closely related to the crystal grain size and the grain boundary condition of hot-pressed alloys. Although the phonon scattering at the fine grain boundary means a low level of thermal conductivity, the increased electrical resistivity (ρ) results in a lower figure of merit (Z) than is found in unidirectional solidified materials.

Semiconductor materials made of rapidly solidified thin bismuth-telluride foil include internal grain boundaries with crystals sufficiently fine to be far more effective in decreasing the thermal conductivity (κ). These grain boundaries are assumed to be cleaner than those of the pulverized powders of ingots in terms of contamination. This clear grain boundary also has less of a deteriorating effect on the carrier mobility of hot-pressed alloys prepared using the rapidly solidified foils. Thermoelectric materials fabricated by this process therefore displayed a high figure of merit (Z).

In this paper, we report on the thermoelectric properties of p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ hot-pressed materials using rapidly

solidified thin foil with particular focus on the effect of the fine microstructure in decreasing the thermal conductivity (κ).

2. Experimental Procedure

The alloy ingots were prepared by melting a mixture of pure Bi, Sb and Te ($\geq 99.99\%$). The raw materials were first placed in a fused silica tube, which was then evacuated below 10^{-2} Pa and sealed with argon by fusing the tube ends. The p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ingots were prepared by melting the raw materials in an argon atmosphere using a rocking furnace. Rapidly solidified foil was then obtained through the single roller melt spinning technique using these ingots. These foils showed a width of 2.0 mm and a thickness ranging from 5 to 15 μm . The rotational speed of the copper roller, meanwhile, of diameter 400 mm, was 41.9 s^{-1} ($2000 \text{ rev min}^{-1}$). Hot-pressed specimens of bismuth- and antimony-telluride alloy were prepared from rapidly solidified foils (non-pulverized), and from pulverized and sieved powders under 53 μm respectively in argon. These thin foils or powders were consolidated through hot-pressing at temperatures ranging from 623 to 773 K in argon for 90 minutes to produce billets with a 26 mm diameter and 8 mm thickness. The compacting pressure was varied from 80 to 400 MPa to investigate its influence on the microstructure and thermoelectric properties.

The thermoelectric properties were evaluated at room temperature along a direction parallel to that of the pressing force. To measure the Seebeck coefficient (α) and thermal conductivity (κ) of the alloy, specimens with dimensions of $4 \times 4 \times 4 \text{ mm}$ were cut out from the hot-pressed alloy sample, subjected to heat and then placed between two copper plates. The thermoelectric motive force (E) was measured after applying a small temperature differential (ΔT) across both ends of the specimen. The Seebeck coefficient (α) was determined from the $E/\Delta T$, while the thermal conductivity (κ) was measured through the static comparison method with transparent SiO_2 as a standard sample in a vacuum of $5 \times 10^{-3} \text{ Pa}$. The relative electrical

Fig. 1 Optical micrograph of rapidly solidified $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ foil cross-section.

resistivity (ρ) was measured using the four-probe technique and thermoelectric properties were evaluated in both types of hot-pressed specimens: those prepared as rapidly solidified foils (non-pulverized) and as pulverized powders using the rapidly solidified foils respectively.

3. Results

An optical micrograph of the foil cross-section of the rapidly solidified $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy is shown in Fig. 1. The photograph shows a columnar grain structure perpendicular to the foil surface, a characteristic microstructure formed during rapid solidification caused by the cooling roller. The width of the grains ranged from 0.5 to 3 μm with an average grain size of 10 μm in the direction of the foil thickness. The fine grain boundaries formed in the foil were expected to be less influenced by oxidation than the pulverized powder surface, since analysis showed the oxygen concentration for foils and pulverized powders to be 220 ppm and 910 ppm respectively. The level of contamination from impurities, caused by the pulverizing process, was also supposed to show up a similar disparity between foils and powders.

To investigate the thermoelectric properties of the hot-pressed specimens of rapidly solidified $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy foils, rapidly solidified foils (non-pulverized) and pulverized powders under 53 μm were prepared in order to evaluate two types of hot-pressed specimens.

The Seebeck coefficients of both types of specimens were then evaluated, through hot-pressing for 90 minutes at 80 MPa. Figure 2 illustrates the variation in Seebeck coefficients (α) of hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys using rapidly solidified foils as a function of the hot-pressing temperature. This result indicates the Seebeck coefficient values were under 200 $\mu\text{V/K}$ for specimens hot-pressed at 623 K. For specimens hot-pressed at temperatures in the range 673 to 773 K however, the Seebeck coefficients (α) indicated values ranging from 220 to 240 $\mu\text{V/K}$, clearly not dependent on the hot-pressing temperature. The relative densities of the specimens hot-pressed at 623 K were 93.7% in the case of pulverized and sieved powders and 96.1% when rapidly solidified (non-pulverized) foils were used. The increase in density corresponding to the increasing hot-pressing temperature reached figures of 98.0% and 99.8% respectively for

Fig. 2 Seebeck coefficient as a function of hot-pressing temperature for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ specimens.

specimens hot-pressed at 773 K.

These results suggest that the hot-pressing process influences the carrier concentration closely related to altered defects, such as vacancies and voids formed during the rapid solidification process and that in addition, the influence of the relative density on the carrier concentration is greater in specimens prepared from pulverized powders than those using rapidly solidified foils.⁷⁻⁹⁾

The electrical resistivity (ρ) and thermal conductivity (κ) of hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys are illustrated as a function of the hot-pressing temperature in Figs. 3 and 4.

Fig. 3 Electrical resistivity as a function of hot-pressing temperature for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ specimens.

Fig. 4 Thermal conductivity as a function of hot-pressing temperature for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ specimens.

Fig. 5 Optical micrographs of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys hot-pressed at (a) 673 K and (b) 773 K using rapidly solidified foils.

Fig. 6 Optical micrographs of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys hot-pressed at (a) 623 K and (b) 773 K using pulverized powders.

The relatively high electrical resistivity (ρ) of the specimen hot-pressed at 623 K using the pulverized powders was, as aforementioned, due to density lower than that of the specimen using rapidly solidified foils. As the hot-pressing temperature increased, the electrical resistivity fell to a value under $1.8 \times 10^{-5} \Omega\text{m}$. In contrast, the electrical resistivity for specimens prepared using rapidly solidified foils increased slightly with temperature, presumably due to the loss of predetermined crystal orientation in foils alongside an increase in the hot-pressing temperature. Figures 5(a) and (b) shows optical micrographs of hot-pressed specimens using rapidly solidified foils at 673 and 773 K. As the grain grew, the predetermined microstructure morphology was lost. As shown in Fig. 4, the thermal conductivity for specimens using rapidly solidified foils was lower than $1.2 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ at hot-pressing temperatures exceeding 673 K while for specimens using pulverized powders, it increased in tandem with higher hot-pressing temperature, a result seemingly dependant on the growth of the crystals. Figures 6(a) and (b) shows optical micrographs of hot-pressed specimens using pulverized powders hot-pressed at 623 and 773 K, with specimens at the higher temperature exhibiting growth of the grain, the reason for the increase in the thermal conductivity (κ) value.

The thermal conductivity (κ) property includes levels of electronic and phonon thermal conductivity, (κ_{el}) and (κ_{ph}) respectively, in a relationship that can be expressed using the following eq. (1):

$$\kappa = \kappa_{\text{el}} + \kappa_{\text{ph}} \quad (1)$$

The values of κ_{ph} decreased due to phonon scattering at the grain boundaries,^{10–14} demonstrating the effectiveness of the fine microstructure in decreasing the thermal conductivity (κ), basically comprising phonon and electronic thermal conductivities: (κ_{ph}) and (κ_{el}).

Both types of specimens demonstrated very low values of thermal conductivity (κ) below $1.1 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ at hot-pressing temperature of 673 K. These low thermal conductivity (κ) values could be due to the fine microstructure obtained in the rapid solidification technique.

In this study on the effect of the hot-pressing temperature, as shown in Fig. 7, the hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys using rapidly solidified foils exhibited a figure of merit up to $3.34 \times 10^{-3} \text{ K}^{-1}$. This high value might be due to the low level of thermal conductivity. The figure of merit (Z) value is given here in eq. (2):

$$Z = \alpha^2 / (\rho\kappa) \quad (2)$$

The figure of merit was relatively low for specimens hot-pressed at 773 K using rapidly solidified foils because of the high electrical resistivity. This result can be explained by the loss in predetermined microstructure and crystal orientation as observed in Fig. 5.

Pressure dependence was also evaluated in both types of specimens, subject to hot-pressing for 90 minutes at 673 K. Figure 8 illustrates the hot-pressing pressure dependence of

Fig. 7 Variations in figure of merit (Z) for hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys prepared by rapidly solidification technique at various hot-pressing temperatures.

Fig. 8 Seebeck coefficient as a function of hot-pressing pressure for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ specimens.

Fig. 9 Electrical resistivity as a function of hot-pressing pressure for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ specimens.

Fig. 10 Thermal conductivity as a function of hot-pressing pressure for $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ specimens.

Seebeck coefficients (α) of hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys using rapidly solidified foils, with only small effects of pressure registered in terms of the Seebeck coefficients (α) for specimens of these materials. On the other hand, as the pressure increased, the Seebeck coefficients (α) increased correspondingly for specimens using pulverized powders. A comparison between these two types of specimens reveals specimens using pulverized powders with reduced Seebeck coefficients and therefore a higher carrier concentration in them.

Figures 9 and 10 show variations in the electrical resistivity (ρ) and thermal conductivity (κ) of hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys as a function of the hot-pressing pressure. As the pressure increased, the electrical resistivity (ρ) also increased slightly for both specimens, something closely related to the decrease in thermal conductivity (κ) caused by the hot-pressing pressure. This tendency for pressure to effect thermal conductivity (κ) and electric resistivity (ρ) demonstrates the presence of a changed carrier mobility. In other words, this is a change in the value of $\kappa\ell$ in eq. (1). This low value of thermal conductivity (κ) is likely due to the fine microstructure obtained through rapid solidification and cleavage of foils under high pressure. The grain boundaries formed here under high pressure during the hot-pressing process acted as a barrier to carrier mobility.

Figure 11 shows an optical micrograph for specimens hot-pressed at 673 K for 90 minutes at 400 MPa, with a very fine

Fig. 11 Optical micrograph of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy hot-pressed at 400 MPa prepared by rapidly solidified foils.

microstructure and grain sizes under $3 \mu\text{m}$ observable. These fine grain boundaries were formed during the hot-pressing process.

As illustrated in Fig. 12, the figure of merit (Z) for hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys was a factor of the hot-pressing pressure. It was noted that pressures exceeding 120 MPa were not preferable for obtaining a high merit value figure. This

Fig. 12 Variations in figure of merit (Z) for hot-pressed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys prepared by rapid solidification technique at various hot-pressing pressures.

limit is due to the high level of electrical resistivity (ρ) relating to decreased carrier mobility caused by the increase in grain boundaries formed during the hot-pressing process. It is reasonable to assume that the hot-pressing pressure affects the carrier scattering and mobility at the grain boundaries.

Even though the pulverizing process of rapidly solidified foils was effective in decreasing levels of thermal conductivity, the crystal orientations formed in the foils were lost. For hot-pressed specimens using foils, the loss of predetermined crystal orientation triggered by increased pressing temperature and pressure led to a decline in the figure of merit. In order to obtain higher thermoelectric properties therefore, further technical improvements are needed to maintain the crystal orientation in foils during the consolidation process.

4. Summary

The thermoelectric properties of hot-pressed specimens using rapidly solidified $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy foils were evaluated and two types of specimens were prepared. The first was a hot-pressed specimen using rapidly solidified foils that were quenched while the other type was a specimen made from pulverized and sieved powders. The temperature and pressure dependence of these specimens were then studied.

The fine microstructure proved extremely effective in lowering the thermal conductivity (κ) and raising the figure of

merit (Z). As the hot-pressing temperature increased, the consequent grain formation caused an increase in thermal conductivity (κ). When pressure exceeding 120 MPa was exerted during the hot-pressing process, this increased the grain boundary and lowered the overall carrier mobility.

The resultant figure of merit (Z) values for the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys reached a maximum of $3.34 \times 10^{-3} \text{ K}^{-1}$ for those specimens hot-pressed at 673 K for 90 minutes at 80 MPa. This result shows that thermoelectric properties for hot-pressed alloys prepared using rapidly solidified foil exhibit considerable improvements over alloys made from conventional materials.

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