

Thermoelectric Properties of N-type 90% Bi₂Te₃+10%Bi₂Se₃ Thermoelectric Materials Produced by Melt Spinning Method and Sintering

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Abstract

N-type Bi₂Te₃-Sb₂Te₃ solid solutions doped with CdCl₂ was prepared by melt spinning, crushing and vacuum sintering processes. Microstructure, bending strength and thermoelectric property were investigated as a function of the doping quantity from 0.03wt.% to 0.10wt.% and sintering temperature from 400°C to 500°C, and finally compared with those of conventionally fabricated alloys. The alloy showed a good structural homogeneity as well as bending strength of 3.88Kg/mm². The highest thermoelectric figure of merit was obtained by doping 0.03wt.% and sintering at 500°C

Keywords : Thermoelectricity, Bi₂Te₃ type alloy, Rapid solidification, Powder Metallurgy, N-type

1. Introduction

CdCl₂ added Bi₂Te₃-Bi₂Se₃ thermoelectric alloys prepared using a directional growing process exhibits an anisotropy in thermoelectric performance and mechanical properties along the (111) direction due to the basal plane existent along the Te-Te layer [1]. Powder metallurgy process (PM) is known for an alternative to modify the intrinsic anisotropy [2]. Among various PM, the milling type process becomes more effective for the p-type material, but n-type due to forming Se segregation in the grain boundary as well as a less inhomogeneity in the microstructure [3]. On the other hand, PM by rapid solidification, which is rarely reported, may be useful, because it is a well known technique for generating homogeneous microstructure in alloys. In addition, the thermoelectric anisotropy corresponding to the unit cell of a large ratio of *c*-axis to *a*-axis can be effectively modified by rapid solidification and vacuum sintering [4].

The aim of this work is to obtain the optimal thermoelectric bulk material of n-type 90% Bi₂Te₃+10%Bi₂Se₃ prepared by a combination of rapid solidification and sintering processes. Microstructure, strength and thermoelectric property were examined as a function of dopant level CdCl₂ and sintering temperature.

2. Experimental and Results

Master alloys of 90%Bi₂Te₃+ 10%Bi₂Se₃ with excess 0.03 to 0.1wt.% CdCl₂ were prepared by heating mixtures of 99.999% pure constituent elements in evacuated quartz ampoules (10⁻⁴ Torr) at 650°C for 30min. Melt spun ribbons

16μm thick and 2μm wide were produced by inductively melting the master alloys under argon atmosphere and ejecting the melt through a bottom hole of 0.5mm in diameter onto the perimeter of a Cu wheel rotating at a surface speed of 47m/s. The brittle ribbons were crushed and cold compacted in a cemented carbide mold at 700MPa, then sintered in a pyrex mold at 400-500°C for 50min. under vacuum of 10⁻⁵Torr.

Thermoelectric properties were measured perpendicular to the compression axis and the electrical resistivity was measured by a standard four points probe method with a dc current of 50mA, having an accuracy of better than 3%. Seebeck coefficient (α) was determined by measuring the temperature and electric potential difference between each end of the specimen [2], in which the temperature gradient along the sample ranged from 0 to 10K.

Room temperature Hall coefficient and Hall mobility was measured by van der Pauw method(5kG, 50mA) and determined using an ac technique with a constant magnetic field in the range of 0.5-0.9T. Thermal conductivity was measured using Harman method at 10⁻⁵ torr to minimize the thermal conduction through convection. The both Hall coefficient and thermal conductivity were measured to within 5% accuracy. These data were used to determine carrier concentration, carrier mobility and the thermoelectric figure of merit.

The strength was measured using three-point bending tests. X-ray diffraction spectrum of RSeD and vacuum sintered n-type alloy indicates a formation of rhombohedral Bi₂Se₃ crystal structure. Determining from the peaks of (0 0 15) and (0 0 18) which are of thermoelectric phases, the melt spun alloy might show good thermoelectric performance. The cast

specimen generally presented an oriented thermoelectric performance depending on the growing direction. Density of the sintered body was increased from 7.3g/cm^3 to 7.43g/cm^3 as the sintering temperature was raised from 400°C to 450°C without any further change between 450°C and 500°C , becoming about 96.5% to the theoretical density of about 7.7g/cm^3 . However, sintering at 550°C induced the reduction, corresponding to the melting of the compound, which begins between 550°C and 600°C [5].

The maximum thermoelectric power (α) of 211, 200 and $182\mu\text{V/K}$ was obtained by sintering at 450°C with doping from 0.03wt.% to 0.10wt.%, respectively. Increasing the sintering temperature to 500°C produces the electrons produces [6], so that the thermoelectric power becomes low in accordance with the equation, $\alpha \approx \gamma - \ln n$, where γ is scattering coefficient and n is carrier concentration [4].

Electrical (EC, open symbols) and thermal (TC, closed symbols) conductivities were increased with increasing the temperature and dopant quantity, resulting in maximum values of $786/\Omega\text{cm}$ and 1.28WmK , respectively, at 500°C and 0.1wt.% CdCl_2 addition. The increases are possibly due to an increase in the carrier mobility (μ) and concentration (n), respectively, given by the equation that $\sigma = n e \mu$ [2]. The carrier concentration becomes rich as the dopant adds and the sintering temperature increases, whereas the carrier mobility will be improved by the enhanced bonding between the melt spun ribbons as the sintering temperature increase.

Thermal conductivity, κ , is written as a sum of the lattice (κ_{ph}) and the electronic (κ_{el}) components, i.e. $\kappa = \kappa_{\text{el}} + \kappa_{\text{ph}}$ [7]. The lattice factor becomes lower in polycrystalline alloy than in the single crystal alloy, while being constant at a fixed composition. It is known that the K_{ph} is inversely proportional to the mass of the unit cell and grain size. In addition, temperature regards as an important factor determining the phonon scattering. The grain size effect is many reported by researchers that minimum thermal conductivity is reached when the phonon mean free path equals to its wavelength. For the long wavelength acoustic waves, the phonon reflection occurs by difference between the acoustic impedance across the interface of grains and materials. K_{el} , however, is directly proportional to the Lorentz constant (L), electrical conductivity (σ) and temperature (T). Thus, the K_{el} increases with increase in the sintering temperature and the dopant addition.

The thermoelectric figure of merit (Z) derived from the thermoelectric measurement data plotted with sintering temperatures and CdCl_2 quantities was measured to be maximum of $2.15 \times 10^{-3}/\text{K}$ at 500°C in case of 0.03wt.% CdCl_2 addition (Fig. 5). This result may correspond to the increase in electrical conductivity and decrease of lattice thermal conductivity.

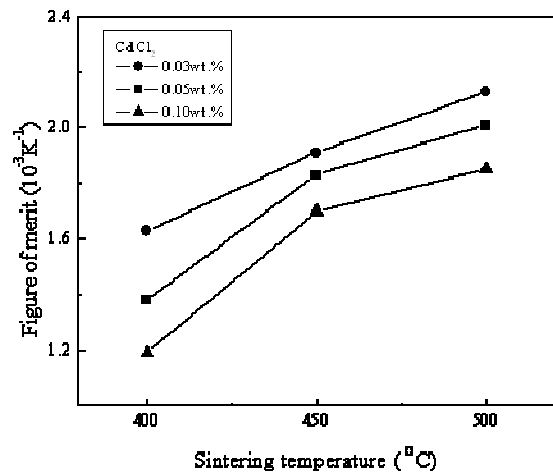


Fig. 5. Thermoelectric figure of merit (Z) of n type $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ alloys.

3. Summary

Thermoelectric n-type 90% Bi_2Te_3 + 10% Bi_2Se_3 bulks were successfully produced by a rapid solidification and vacuum sintering processed. The as spun ribbon consists of homogeneous $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ solid solution compounds and further exhibits a sound theoretical density of 96.5% by vacuum sintering at 450°C and 500°C . Due to good bonding between the homogeneous ribbons at 500°C and electron production reaction, both electric and thermal conductivity were simultaneously improved while the thermoelectric power was deteriorated with the sintering temperature and the dopant quantity. The highest figure of merit of $2.15 \times 10^{-3}/\text{K}$ was obtained at 500°C and 0.03wt.% CdCl_2 addition.

4. References

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