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Thermal and microstructure simulation of thermoelectric material Bi_2Te_3 grown by zone-melting technique

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ABSTRACT

The thermoelectric conversion efficiency of the thermoelectric material Bi_2Te_3 is significantly affected by its microstructure because of its anisotropy. In this study, the zone-melting technique is used to grow Bi_2Te_3 columnar crystals. The zone-melting process directionally solidifies and purifies an ingot by a moving a heater along the ingot. For predicting the temperature variation and distribution in the crystallization process and the microstructures of Bi_2Te_3, a zone-melting model is developed and numerical simulation techniques are used. The simulation results are compared with experimental measurements to verify the numerical model. The verified numerical model is used to investigate the optimal process parameters. The process parameters, namely the temperature of the heater and the movement speed of the heater and the cooling devices, are adjusted in order to obtain good-quality columnar crystals. The shapes of the solidification interface, which greatly affect the direction of grain growth and the grain size, are compared.

1. Introduction

The development of thermoelectric materials is an integral part of green energy. Recently, the trend has been to use thermoelectric effects to transform waste heat into electric power. The fundamental phenomenon of thermoelectric effects is the Seebeck effect [1]. In 1823, Seebeck observed that if two different conductors constituted a loop and the junctions of these two conductors were held at different temperatures, then a voltage difference (ΔV), which was proportional to the temperature difference (ΔT), was created. The Seebeck coefficient (S) is defined as the voltage difference generated by 1 K. The Seebeck coefficient is given as:

$$S = \frac{\Delta V}{\Delta T} \quad (1)$$

The conversion efficiency of thermoelectric devices depends on the performance of thermoelectric materials. The performance can be evaluated via the thermoelectric figure of merit, abbreviated as ZT [2]. ZT is defined as:

$$ZT = \frac{S^2 \sigma}{\kappa} \quad (2)$$

where σ is the electrical conductivity and κ is the thermal conductivity. A higher ZT value indicates better thermoelectric performance. Generally, Bi_2Te_3 has a high ZT value (~ 1) at room temperature. Bi_2Te_3 was thus selected in this study.

Bi_2Te_3 has a rhombohedral crystal structure with five atoms per unit cell. Because of its high anisotropy, the electrical and thermal conductivities at the direction perpendicular to c axis are four and two times larger, respectively, than those at other directions. Therefore, the ZT value is highest at the direction perpendicular to c axis. The layers are bound by the van der Waals force. Bi_2Te_3 single crystal is easily been split along the basal plane [2]. In order to improve the mechanical properties, the directional growth method was used to grow Bi_2Te_3 polycrystals. The objective was not only to improve machinability but also to grow columnar crystals for maintaining high anisotropy. Anisotropy affects the electrical and thermal properties, and thus the columnar crystal structure can improve the thermoelectric conversion efficiency by increasing the electrical conductivity σ and reducing the thermal

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conductivity κ since $ZT = S^2\sigma T/\kappa$. Bi_2Te_3 columnar crystals were prepared via the zone-melting method in this study.

In industry, 17 φ and 25 φ Bi_2Te_3 ingots are effectively prepared via the zone-melting method, with cross-sectional diameters of 17 mm and 25 mm, respectively. However, it takes almost one day for one crystal growth. For mass production, the size of the Bi_2Te_3 ingot must be increased. The current objective is to grow 30 φ Bi_2Te_3 ingots. The process parameters, namely the temperature of the heater and the movement speed of the heater and the cooling devices, should be adjusted in order to maintain the quality of columnar crystals. However, determining suitable process parameters for 30 φ Bi_2Te_3 ingots experimentally is expensive.

In this study, computer simulations were used to simulate the temperature variation and distribution of the zone-melting process and the microstructures of 30 φ Bi_2Te_3 ingots. The 17 φ ingot zone-melting temperature field simulation model was used for thermal verification. The verified thermal simulation parameters were input into the 25 φ ingot zone-melting temperature field simulation model and verified using another verification method. Then, the 25 φ ingot zone-melting temperature field simulation model was coupled with the cellular automata finite element (CAFE) model to simulate the microstructure of 25 φ Bi_2Te_3 ingots, which was verified with the experimental microstructure. The thermal and microstructure parameters were verified to obtain reliable simulation parameters for the 30 φ ingot zone-melting simulation model. Finally, the 30 φ ingot zone-melting simulation model was used to investigate the optimal process parameters.

2. Experimental method

Appropriate amounts of high-purity (99.99%) Bi and Te were weighed to make Bi_2Te_3. The inside wall of the quartz tube was carbon-coated by acetone cracking. Bi and Te (in a vacuum quartz tube) were melted in a rocking furnace to ensure composition homogeneity. Then, Bi_2Te_3 alloys were grown via the zone-melting method at temperatures of 710–770 °C and movement speeds of 0.75–1.75 cm/h for the heater and cooling devices. A schematic diagram of the zone-melting method is shown in Fig. 1. Bi_2Te_3 was encapsulated by quartz and put inside the annular heater and cooling devices. The annular heater and cooling devices moved with time. The experimental parameters used in this study are shown in Table 1.

2.1. *Verification method of 17 φ ingot temperature field simulation model*

Based on the safety consideration of released Te vapor, two 1.6 φ quartz tubes were settled at the bottom of the 17 φ quartz tube and treated with high temperature and quenching treatment, allowing the 1.6 φ and 17 φ quartz tubes to fully engage. Then, the thermocouples were placed inside the 1.6 φ quartz tubes and the Bi_2Te_3 temperature across the quartz tubes was measured, as shown in Fig. 2.

2.2. *Verification method of 25 φ ingot temperature field simulation model*

The thermocouples (k-type) were directly put inside the 25 φ quartz tube from the top, and the tails of the thermocouples were fixed at specific locations for measuring Bi_2Te_3 temperature. The top of the quartz tube was sealed with heat-resistant sealant. Another quartz tube was connected at the upper section of the 25

Table 1
Experimental parameters of zone-melting process.

Casting material	Crucible/ mould	System initial temperature (°C)	Heater temperature (°C)	Cooler temperature (°C)	Movement speed (cm/h)
Bi_2Te_3	Quartz	30	710–770	30	0.75–1.75

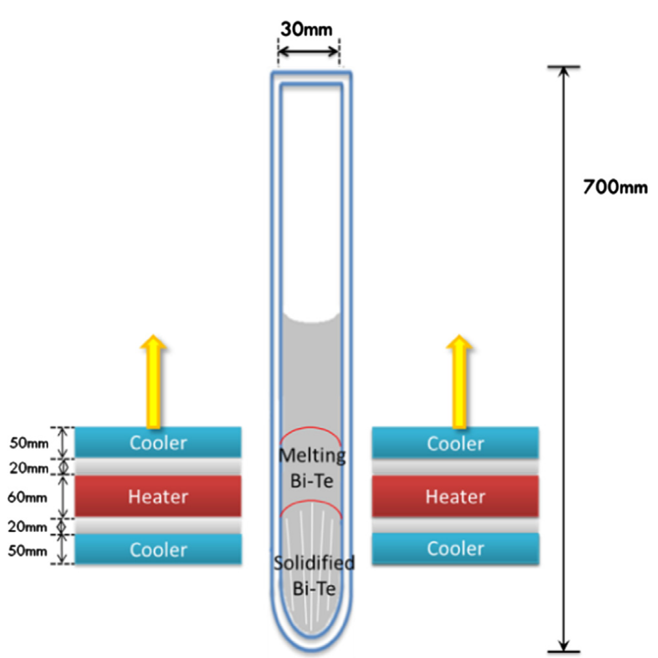

Fig. 1. The schematic diagram of zone-melting method.

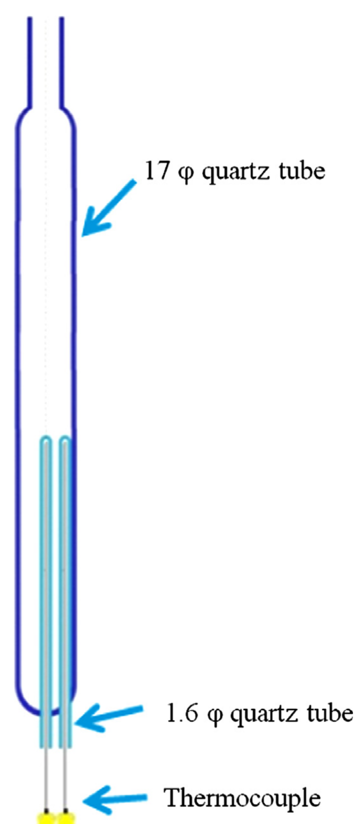

Fig. 2. Verification method of 17 φ temperature field simulation model.