A numerical study of zone-melting process for the thermoelectric material of Bi$_2$Te$_3$

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Abstract. In this study, a numerical model has been established by employing a commercial software; ProCAST, to simulate the variation/distribution of temperature and the subsequent microstructure of Bi$_2$Te$_3$ fabricated by zone-melting technique. Then an experiment is conducted to measure the temperature variation/distribution during the zone-melting process to validate the numerical system. Also, the effects of processing parameters on crystallization microstructure such as moving speed and temperature of heater are numerically evaluated. In the experiment, the Bi$_2$Te$_3$ powder are filled into a 30mm diameter quartz cylinder and the heater is set to 800°C with a moving speed 12.5 mm/hr. A thermocouple is inserted in the Bi$_2$Te$_3$ powder to measure the temperature variation/distribution of the zone-melting process. The temperature variation/distribution measured by experiment is compared to the results of numerical simulation. The results show that our model and the experiment are well matched. Then the model is used to evaluate the crystal formation for Bi$_2$Te$_3$ with a 30mm diameter process. It’s found that when the moving speed is slower than 17.5 mm/hr, columnar crystal is obtained. In the end, we use this model to predict the crystal formation of zone-melting process for Bi$_2$Te$_3$ with a 45 mm diameter. The results show that it is difficult to grow columnar crystal when the diameter comes to 45mm.

1. Introduction

The green energy technology is always the hot issue in the field of science and engineering. The thermoelectric material plays an important role in green energy technology [1]. The thermoelectric conversion efficiency depends on the figure of merits (ZT value) of itself [2]. In this study, Bi$_2$Te$_3$ is chosen because of its high ZT value at ambient temperature and are frequently applied to thermoelectric module for power generation [3,4]. Bi$_2$Te$_3$ showed high anisotropy and said to have higher ZT value perpendicular to the c axis [1,5]. In order to keep its anisotropy to acquire high ZT value, big columnar grain structure should be produced. With big columnar grain, electrical conductivity will be enhanced and thermal conductivity will be reduced. Thus ZT value will be enhanced. In this study, zone-melting which is a unidirectional solidification process is chosen to manufacture the Bi$_2$Te$_3$. In the industry, cylindrical ingot with 17mm and 25mm diameter can be mass produced. But the manufacturing time of zone-melting is long which is around a day. So increase ingot’s diameter is the way to raise the output of Bi$_2$Te$_3$. But temperature field will change with increasing diameter of Bi$_2$Te$_3$. With an aim to maintain the quality of bigger ingot, the processing parameters must be adjusted. It is expensive to use experimental method to find the processing
parameters leading to big columnar grain because of the high price of Bi$_2$Te$_3$. So this study uses numerical method to acquire the processing parameter which lead to big columnar grain which make Bi$_2$Te$_3$ have high thermoelectric conversion efficiency.

2. Mathematical and Experimental method

The most important part of this study is to validate the simulation system. The simulation system will be validated by temperature field distribution and microstructure. In temperature part, an experiment is conducted to measure temperature profile during the zone-melting process which will be compared with the temperature profile of simulation. A k-type thermocouple is inserted into the quartz tube which is filled with Bi$_2$Te$_3$ powder to measure the temperature field during the melting and solidification process as showed by Fig.1. Then, the experimental microstructure will be compared with the results of simulation, too. Following are mathematical methods used in this simulation system.

2.1 Heat transfer module

In this study, convection and mass transfer are not considered. The heat transfer mechanism of zone-melting process is dominated by conduction and radiation. The equations used in heat transfer in this system are as follows

\[ \rho C_p \frac{dT}{dt} = \lambda \nabla^2 T + \rho \Delta H \frac{df_s}{dt} \]  

[1]

\[ -k_a (n \cdot \nabla T) = h (T - T_a) + \varepsilon_a \sigma (T^4 - T_a^4) \]  

[2]

This (2-1) is revised from Fourier’s fundamental laws of heat transfer to calculate the three-dimension temperature field during zone-melting process, where $\rho$ is the density, $C_p$ is the heat capacity under constant pressure, $\lambda$ is the thermal conductivity, $H$ is the latent heat and, $f_s$ is the solid fraction of the material used. The (2-2) [6] is the radiation part, derived by energy balance where $h$ is the heat transfer coefficient, $\varepsilon_a$ the thermal emissivity of the quartz, $\sigma$ is the Stefan-Boltzmann constant, and $T_a$ is the effective ambient temperature. The whole heat transfer mechanisms in the system are as Fig 2. The heat is transfer from heaters into the quartz tube and Bi$_2$Te$_3$ by radiation. Then the heat is transfer from the Bi$_2$Te$_3$ to the cooler and air by radiation or through conduction of Bi$_2$Te$_3$ in the cooling process. The parameters used in simulation are listed in Fig 3.

![Figure 1. Experimental setup](image)
2.2 Microstructure (CAFÉ module)

In this study, simulation of microstructure is based on the macroscopic temperature result. Numerical simulation of microstructure is according to CA (cellular automaton) method [7, 8, 9], which is developed by Rappaz and Gandin. CA method use deterministic model to calculate the growth rate of dendrite and use probabilistic model to deal with the distribution of nuclei and direction of growth. This method is based on heterogeneous nucleation model and continuous nucleation model. Then use Gaussian distribution as a relation between nucleation density and undercooling which is governed by (3-3) and (3-4) and showed by Fig. 4.

\[
n(\Delta T) = \int_0^{\Delta T} n \left( \frac{dn}{d(\Delta T')} \right) d(\Delta T') [1 - f_s(\Delta T')] d(\Delta T')
\]  

(3)

**Figure 2.** Heat transfer mechanism and dimensions of setup

**Figure 3.** Parameters used in simulation
where \( n(\Delta T) \) is density of grain, \( f_c(\Delta T') \) is solid fraction, \( n_{max} \) is the maximum density of nuclei, \( \Delta T_n \) means nucleation undercooling, and \( \frac{dn}{d(\Delta T')} \) is found according to the Gaussian distribution. The calculation of this microstructure module is based on the result of heat transfer module because the undercooling has a large impact on nucleation. When the heater go through the Bi\textsubscript{2}Te\textsubscript{3}, the Bi\textsubscript{2}Te\textsubscript{3} melt firstly. Then melted Bi\textsubscript{2}Te\textsubscript{3} will be cooled by radiation and conduction. In this time, undercooling occurs, resulting in the nucleation and grain growth.

\[
\frac{dn}{d(\Delta T')} = \frac{n_{max}}{\sqrt{2\pi}(\Delta T_n)} \exp \left[ -\frac{1}{2} \left( \frac{\Delta T' - \Delta T_n}{\Delta T_n} \right)^2 \right]
\]

Figure 4. The relation between nucleation density and undercooling.

When the undercooling reaches nucleation conditions, specific CA cells start to nucleate. In a time step \( \delta t \), temperature of a component reduces \( \delta T \), then the undercooling increases \( \delta(\Delta T) \). At this time, new grain density of nucleation on the liquid metal surface showed as (2-5):

\[
\delta n = n_0(\Delta T - \delta(\Delta T)) - n_0(\Delta T) = \int_{\Delta T}^{\Delta T + \delta(\Delta T)} \frac{dn}{d(\Delta T')} d(\Delta T')
\]

In other words, it will give a site and direction of nucleation by random as the basis of following growth of grain. In the heterogeneous nucleation part, the relation between nucleation density and undercooling is explained by Gaussian distribution theory. In the grain growth part, growth rate is calculated using Kurz-Giovanola-Trivedi (KGT) model which is governed by (2-6)

\[
\nu = a_2\Delta T^2 + a_3\Delta T^3
\]

Where \( \nu \) is the growth rate, \( a_2 \) and \( a_3 \) are growth kinetic parameters dependent upon the composition of the alloy.

| CA cell size (micrometers) | Nb. Crystallographic orientation | Volume nucleation |
|-----------------------------|---------------------------------|-------------------|
| 100                         | 5000                            | \( \Delta T_n \)  |
|                              |                                 | \( \Delta T_\sigma \) |
|                              |                                 | \( N_{max} \)      |
| 10                          | 0.05                            | 7.5x10\textsuperscript{7} |
| Nb. Cell in a block         | Seed random number              | Surface nucleation |
| 10x10x10                    | 100                             | \( \Delta T_n \)  |
|                              |                                 | \( \Delta T_\sigma \) |
|                              |                                 | \( N_{max} \)      |
| 1                           | 0.05                            | 2.5x10\textsuperscript{5} |

Figure 5. Parameters used in simulation (\( \Delta T_n \): averaged undercooling, \( \Delta T_\sigma \): standard deviation of undercooling, \( N_{max} \): maximum grain density)
3. Results and Discussions

It is important to verify the accuracy of model when using numerical method to simulate manufacturing process. In this study, the experimental parameter are as follows: Heater is heated up to 770°C in first 30 minutes, then heated to 800°C from 30 to 60 minutes. After 60 minutes, the heater is fixed at 800°C to the end of the process. The heater starts to move up along the quartz tube with a moving speed of 1.25 cm/hr from 120 minutes to the end of the process. The parameters of simulation are all the same with the experimental parameters. The results of validation showed on Fig. 6.

The results show that the trend of temperature is nearly the same. There is some area with big difference from 600°C to 800°C of heating up part. This part is acceptable because the most concerned part of the curve is the solidification area which is related to the following microstructure. That is, the part pointed by blue circle on the Fig. 6 which is well matched. The solidus temperature and liquidus temperature are 530°C and 586°C respectively. In other words, the range between...
solidus temperature and liquidus temperature is completely located in the well matched part. In other words, the heat transfer module is validated and said to have enough confidence in predicting the temperature field of the zone-melting process. Fig. 7 is the temperature profile of whole specimen with the change of time. Then the validated heat transfer module is applied to the following microstructure module. The morphology of experimental grain is compared to the simulated grain. The results of Fig. 7 and Fig. 8 showed that they both have tendency of columnar grain and the grain size also have the same tendency from the bottom to top of the Bi$_2$Te$_3$ ingot. And this microstructure module has been used to predict the morphology at different processing parameters. It’s found that when the moving speed is slower than 17.5 mm/hr, columnar crystal is obtained. Then a 45 mm model is build which is using the same grain growth parameters to predict the morphology of grain. The results showed that it is hard to produce big columnar grain when the ingot comes to 45 mm because the cooling is not as homogeneous as the 30 mm manufacturing process.

**Figure 8.** The longitudinal section morphology of the experimental and simulation with same processing parameters, heater is set to 800°C with a moving speed of 12.5 mm/hr.

**Figure 9.** The transverse section morphology of simulation with processing parameters, heater is set to 800°C with a moving speed of 12.5 mm/hr.

### 4. Conclusion
A validated numerical model is been built to predict the temperature field and following microstructure of 30 mm Bi$_2$Te$_3$ manufacturing by zone-melting process. It’s found that when the moving speed is slower than 17.5 mm/hr, columnar crystal is obtained. In the end, we use this model to predict the crystal formation of zone-melting process for Bi$_2$Te$_3$ with a 45mm diameter. The results show that it is difficult to grow columnar crystal when the diameter comes to 45mm.

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