Microstructure and properties of n-type Bi$_2$Te$_3$-based thermoelectric material fabricated by selective laser sintering

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Abstract

An n-type Bi$_2$Te$_3$-based thermoelectric material Bi$_2$Te$_{2.85}$Se$_{0.15}$ was prepared through an SLS (Selective Laser Sintering) process with E12/Bi$_2$Te$_{2.85}$Se$_{0.15}$ as composite powder (weight ratio 1:7), from which E12 was degreased after the SLS process. It was studied the effect of laser power, scanning speed and scanning interval on the density and thermoelectric properties of the sintered samples. The laser power was found the most important in influencing factor, while the scanning interval was the second and the scanning speed the least. The maximum dimensionless thermoelectric figure of merit $ZT$ is about 0.88 in the condition when the laser power, scanning interval and scanning speed were 20 W, 0.26 mm and 3000 mm s$^{-1}$, respectively.

1. Introduction

Thermoelectric materials, which can convert heat into electricity directly, are environment friendly [1]. It is believed that they have bright application prospects because of their advantages of high reliability and long noiseless and pollution-free operational lifetime. However, they fail to be widely used in practice due to their low conversion efficiency [2, 3], Which is always measured by a dimensionless figure of merit $ZT$. Specifically, $ZT$ is defined as $ZT = \alpha^2\sigma T / \kappa$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity and $T$ is the absolute temperature [4, 5].

Bi$_2$Te$_3$-based thermoelectric materials have larger Seebeck coefficient and lower thermal conductivity compared with other types of thermoelectric materials at near room temperature. They are thus widely used in refrigeration and temperature control area [6, 7]. At present, the main methods to fabricate these materials are limited to spark plasma sintering (SPS) and hot pressing sintering (HPS) [8–11]. This paper deals with application of a dedicated fabrication method of SLS, a rapid prototyping (RP) technique for powder materials, such as glass powders [12], ceramic powders [13] and glass-ceramic powders [14], etc. In contrast to other approaches, it has significant unique advantages, especially in that the forming process is very simple with no fixture required. A composite powder mixed by E12 (as the binder) and Bi$_2$Te$_{2.85}$Se$_{0.15}$ with a weight ratio of 1:7 is adopted for the SLS process. The effects of laser power, scanning speed and scanning interval on the microstructure and properties of the materials are investigated and the optimum laser sintering parameters are identified in this study.

2. Materials and methods

2.1. Experimental materials

The Bi$_2$Te$_{2.85}$Se$_{0.15}$ powder was purchased from Beijing Dream Material Technology Co. Ltd, with purity of 99.99% and density of 6.87 g cm$^{-3}$. The average particle size is 6.875 $\mu$m as shown in figure 1(a). The binder, E12...
epoxy resin as shown in figure 1(b), has an average particle size about 10 μm and density of 0.98 g cm$^{-3}$. E12 epoxy resin has the advantages of low melting point, good bonding property and small heat shrinkage. It is very suitable to be used as binder for SLS process.

2.2. Experimental methods

The flowchart of the forming process is shown as in figure 2. The composite powder with a ratio of 1:7 was first mechanically mixed in a QM-WX4 horizontal planetary ball mill. Then it was transferred into the HK P320 SLS equipment (Huake 3D Technology Co. Ltd, China) for sintering with argon gas protection. The laser source is a continuous CO$_2$ laser and the thickness of the powder layer is 0.10 mm. The laser sintering blocks were placed in a vacuum sintering furnace for degreasing treatment. Relative density of the samples prepared is adopted to evaluate the forming quality. The material fracture morphology, thermal conductivity, electrical conductivity and Seebeck coefficient are adopted to evaluate the forming properties.
The detailed steps for preparing E12/Bi2Te2.85Se0.15 composite powder are depicted as follows: Firstly, a certain amount of n-type Bi2Te2.85Se0.15 thermoelectric material powder and E12 epoxy resin binder (its mass fraction are 10%, 12.5%, 15%, 17.5% respectively) were put into the QM-WX4 horizontal planetary ball mill. Then, the mixing balls were put into the mill with a volume ratio of the mixing ball and the powder being set at 1:3. The E12/Bi2Te2.85Se0.15 composite powder was then finally achieved after running 2 h for the ball mill to make the powder fully mixed. The coefficient of variation method [15] was used to ensure that the mixtures

Table 1. The orthogonal experimental results.

| Sample No. | Laser power/W | Scanning speed/(mm·s⁻¹) | Scanning interval/mm | Relative density/% |
|------------|---------------|--------------------------|----------------------|-------------------|
| 1#         | 18            | 2700                     | 0.26                 | 60.10             |
| 2#         | 18            | 3000                     | 0.28                 | 59.47             |
| 3#         | 18            | 3300                     | 0.30                 | 59.12             |
| 4#         | 20            | 2700                     | 0.28                 | 60.71             |
| 5#         | 20            | 3000                     | 0.30                 | 59.62             |
| 6#         | 20            | 3300                     | 0.26                 | 60.31             |
| 7#         | 22            | 2700                     | 0.30                 | 61.40             |
| 8#         | 22            | 3000                     | 0.26                 | 63.30             |
| 9#         | 22            | 3300                     | 0.28                 | 61.11             |

The detailed steps for preparing E12/Bi₂Te₂.₈₅Se₀.₁₅ composite powder are depicted as follows: Firstly, a certain amount of n-type Bi₂Te₂.₈₅Se₀.₁₅ thermoelectric material powder and E12 epoxy resin binder (its mass fraction are 10%, 12.5%, 15%, 17.5% respectively) were put into the QM-WX4 horizontal planetary ball mill. Then, the mixing balls were put into the mill with a volume ratio of the mixing ball and the powder being set at 1:3. The E12/Bi₂Te₂.₈₅Se₀.₁₅ composite powder was then finally achieved after running 2 h for the ball mill to make the powder fully mixed. The coefficient of variation method [15] was used to ensure that the mixtures
produced are homogeneous and the mixing uniformity $M$ of the composite is 96%. Through a series of trials, we found that the best mass fraction of E12 epoxy resin is 12.5%.

2.3. Properties measurement

The SLS samples prepared are rectangular-shaped with average dimensions of $4 \text{ mm} \times 4 \text{ mm} \times 20 \text{ mm}$ or cylindrical-shaped with average dimensions of $\Phi 12.7 \text{ mm} \times 3 \text{ mm}$ as shown in figure 3. Indirect selective laser sintering method was used to guarantee the forming quality of the powder composite. As the melting temperature of E12 epoxy resin is low, and with the increase of the temperature due to laser irradiation, the flow speed of the melted resin is accelerated. After melting and solidifying, the composite powder is cooled down and bonded together. During the whole sintering process, the composite powder is put on the platform flatly, and the surface of the formed sample is flat and smooth, and the size accuracy is high. The density was measured by Archimedes method. The fracture morphology was analyzed by JSM-5610LV electronic scanning microscope. The electric conductivity $\sigma$ and Seebeck coefficient $\alpha$ were determined with the help of ZEM-3 thermoelectric performance analysis system. The thermal diffusivity $\gamma$ and specific heat capacity $C$ were tested by LFA457 thermal conductivity testing instrument and DSC8500 differential scanning calorimetry, respectively. Then, the thermal conductivity are calculated according to the formula $\kappa = \gamma \cdot \rho \cdot C$, where $\kappa$ is the thermal conductivity and $\rho$ is the density.
Table 2. Relative density before and after degreasing.

| Sample No. | 1#  | 2#  | 3#  | 4#  | 5#  | 6#  | 7#  | 8#  | 9#  |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Relative density before degreasing/% | 60.10 | 59.47 | 59.12 | 60.71 | 59.62 | 61.31 | 61.40 | 63.30 | 61.11 |
| Relative density after degreasing/% | 79.55 | 77.82 | 77.66 | 79.90 | 78.04 | 80.27 | 80.47 | 82.13 | 81.25 |
| Rate of change/% | 19.45 | 18.35 | 18.54 | 19.19 | 18.42 | 19.96 | 19.07 | 18.83 | 20.14 |
Table 3. Thermoelectric parameters results when temperature is at 300 K.

| Sample No. | Laser power/W | Scanning speed/mm · s⁻¹ | Scanning interval/mm | Results                  |
|------------|---------------|--------------------------|----------------------|-------------------------|
|            |               |                          |                      | Thermal diffusivity/mm² · s⁻¹ | Electric conductivity/10³ S · m⁻¹ | Seebeck coefficient/μV · K⁻¹ |
| 1#         | 18            | 2700                      | 0.26                 | 0.193                   | 30.55                         | −137.0                      |
| 2#         | 18            | 3000                      | 0.28                 | 0.203                   | 31.02                         | −136.0                      |
| 3#         | 18            | 3300                      | 0.30                 | 0.210                   | 30.61                         | −134.5                      |
| 4#         | 20            | 2700                      | 0.28                 | 0.187                   | 32.46                         | −140.8                      |
| 5#         | 20            | 3000                      | 0.30                 | 0.196                   | 32.33                         | −139.4                      |
| 6#         | 20            | 3300                      | 0.26                 | 0.179                   | 32.94                         | −141.7                      |
| 7#         | 22            | 2700                      | 0.30                 | 0.172                   | 34.27                         | −144.6                      |
| 8#         | 22            | 3000                      | 0.26                 | 0.154                   | 34.70                         | −146.5                      |
| 9#         | 22            | 3300                      | 0.28                 | 0.166                   | 34.32                         | −145.1                      |
3. Results and discussions

3.1. Laser sintering results

Figure 4 shows the SEM image of E12/Bi2Te2.85Se0.15 composite powder prepared by mechanical mixing method [16, 17]. As shown in figure 4, compared with the original n-type Bi2Te2.85Se0.15 powder, the composite after experiencing mechanical mixing is more like a collection of spherical balls, the surface of which is evenly wrapped by E12 particulates.

The mixed composite powder of E12/Bi2Te2.85Se0.15 was then subject to selective laser sintering. The main process parameters of selective laser sintering include laser power, scanning speed, layer thickness, scanning interval and scanning mode. These parameters directly influence the temperature distribution of the composite powder in processing layer and the quality of the products finally sintered.

The preheating temperature in the forming process has a great influence on the properties of the experimental samples. Warpage deformation is easy to occur when the temperature is too low, and binder may decompose when the temperature is too high, which leads to poor bonding effectiveness [14]. Differential thermal analysis was conducted to obtain the glass transition temperature of E12 epoxy resin. From the testing results, the glass transition temperature of E12 epoxy resin is 79.7 °C. The preheating temperature should be lower than the glass transition temperature. After a number of times of trials, it was found that the forming quality will be satisfactory when the preheating temperature is set at 40 °C.

During laser sintering process, the laser energy density directly affects the forming quality. The laser energy density \( q \) is defined as \( q = P / (S \cdot v) \), where \( P \) is the laser power, \( S \) is the scanning speed and \( v \) is the scanning interval [18]. Therefore, laser power, scanning speed and scanning interval are the important factors that influence the laser energy density. In order to investigate the influence of these three factors on powder forming, an orthogonal experiment of three factors and three levels was designed. According to [19], the reasonable scanning speed ranges from 2700 mm s\(^{-1}\) to 3300 mm s\(^{-1}\). The reasonable variation range of the laser scanning power can be then roughly estimated. Finally in this design, the three levels are set at 18 W, 20 W and 22 W for the laser powers, 2700 mm s\(^{-1}\), 3000 mm s\(^{-1}\) and 3300 mm s\(^{-1}\) for the scanning speeds and 0.26 mm, 0.28 mm...
and 0.30 mm for the scanning interval. The relative density of the samples after experiencing the SLS process is shown in table 1.

3.2. Degreasing results

The DTG/TG analysis for E12 epoxy resin was carried out with a heating rate of 10 °C min⁻¹ and the protection of N₂ being applied. According to the DTG/TG curves as shown in figure 5, the E12 epoxy resin begins pyrolysis reactions when the temperature reaches 300 °C. When the temperature is lower than 300 °C, the thermal weight losing is mainly due to water evaporation. Most of the thermal weight losing occurs when the temperature is between 300 °C and 520 °C. The thermal weight losing becomes weak when the temperature is higher than 520 °C, and the epoxy resin only constantly releases CO, CO₂, CH₄ and other small molecular substances. Its weight keeps almost no change when the temperature is further higher than 800 °C.

It is well known that if the sintering temperature is too low, the epoxy resin does not reach the pyrolysis temperature and the sintering effect is poor and on the other hand if the sintering temperature is too high, the sample is prone to melt and collapse, which will damage the original shape [20]. Since the melting point of Bi₂Te₂.₈₂Se₀.₁₈ material is 585 °C, the degreasing process is defined as shown in figure 6. According to figure 6, the degreasing treatment experiments of the samples were carried out in a vacuum sintering furnace. Firstly, the heating rate was set at 2 °C min⁻¹ from room temperature to 360 °C. Then, the temperature maintained at 360 °C for 1 h for heat preservation, after which the heating rate was changed to 1.5 °C min⁻¹ from 360 °C to 500 °C. What further follows is heat preservation again at 500 °C for 2 h, and it was finally cooled down to room temperature in the furnace as shown in figure 7.

During the degreasing process, as the temperature rises, the binder decomposes and permeates from the samples constantly. The diffusion occurs simultaneously, which makes the sample contracting and the internal pores decreasing constantly [21]. AS porosity is inevitable and the smaller the porosity is, the higher the material density is and the higher its strength. Therefore, the relative density, calculated according to the ratio of actual density to theoretical density, was improved to some extent after degreasing. As is shown in table 2, it increases about 20% and reaches to 80% compared with that before degreasing.
3.3. Microstructural evaluation
Figures 8(a) and (b) show the fracture morphology of 8# sample before and after degreasing respectively. As shown in figure 8(a), the inter-particle cohesion of the sintered sample before degreasing looks good, but there are many pores and thus its relative density is rather low. Figure 8(b) shows the inter-particle cohesion of the sintered sample after degreasing. Apparently, the pores are significantly reduced. The microstructural evolution depicted above demonstrates that the degreasing treatment carried out at a temperature slightly below the melting point of Bi$_2$Te$_{2.85}$Se$_{0.15}$ material can greatly improve the inter particle cohesion, relative density and mechanical strength.

3.4. Thermoelectric properties
To study the thermoelectric properties of the degreased samples, their thermal diffusivity $\gamma$, electric conductivity $\sigma$ and Seebeck coefficient $\alpha$ were measured while the testing temperatures ranges from 300 to 500 K with an interval of 50 K. The results are shown in table 3.

According to the thermal conductivity calculation formula $\kappa = \gamma \cdot \rho \cdot C$, once we measured the specific values of thermal diffusivity $\gamma$, density $\rho$ and heat capacity $C$ at different temperatures, we could be informed the trend how thermal conductivity changes with temperature. Based on the testing data as shown in table 3, we calculated the corresponding thermal conductivity for the degreased samples.

To more comprehensively read the testing results, we calculated thermal conductivity, electric conductivity and Seebeck coefficient by the orthogonal analysis method. The Seebeck coefficient is calculated by direct measurement method $S = \lim_{\Delta t \to 0} \Delta V / \Delta t = dV / dt$, where $\Delta V$ is the potential difference at both ends of the conductor, $\Delta t$ is the temperature difference at the contact point at both ends of the conductor [22]. Figures 9 to 11 shows the relevant thermoelectric performance curves corresponding to each influential factor in different testing temperature conditions. As can be seen from figures 9–11, if arranged in the order of significance and importance, the three factors which affect the thermoelectric performance are laser power, scanning interval and scanning speed. Since the scanning speed has little effect on thermoelectric performance, the three curves in figure 9(b), figures 10(b) and 11(b) are very close, especially the curve of level 1 almost coincided with the curve of level 3 in figure 9(b). For thermoelectric materials, the thermoelectric merit changes inversely with thermal
conductivity. The lower the thermal conductivity, the higher the energy conversion efficiency of the thermoelectric materials, which conforms to the formula \( ZT = \frac{\alpha^2 \sigma T}{\kappa} \) [23]. As can be seen in figure 9, with the increase of the testing temperature beginning from room temperature, the thermal conductivity of the testing samples are slightly decreased at first and then increased. When the laser power A is at level 3, scanning speed B is at level 2 and scanning interval C is at level 1, the composites have least thermal conductivity. Therefore, from the viewpoint of the thermal conductivity, the optimum parameters are A3B2C1.

The thermoelectric merit ZT varies directly with electric conductivity. The greater the electric conductivity, the higher the energy conversion efficiency of the thermoelectric materials. As can be seen from figure 10, when the laser power A is at level 1, the composites have greatest electric conductivity. The influence of scanning speed and scanning interval to electric conductivity is of little significance. With the increase of the testing temperature, the electric conductivity of the samples decreases gradually. The thermoelectric merit varies directly with the square of Seebeck coefficient. The greater the Seebeck coefficient, the higher the energy conversion efficiency of the thermoelectric materials. As can be seen from figure 11, the Seebeck coefficients of all samples are negative, which reveals a unique characteristic for n-type semiconductor material. With the increase of the testing temperature, the absolute values of the Seebeck coefficients increase at first and then decrease. When the laser power A is at level 3, scanning speed B is at level 2 and scanning interval C is at level 1, the composites have greatest Seebeck coefficient. Therefore, from the viewpoint of Seebeck coefficient, the optimum parameters are A3B2C1.

From the above measurement results of relevant thermoelectric properties, the thermoelectric merit ZT for each testing sample at different temperatures was calculated according to the formula \( ZT = \frac{\alpha^2 \sigma T}{\kappa} \). Figure 12 shows the curves describing how thermoelectric merit ZT varies with the testing temperature corresponding to different levels of different influential factors. As can be seen from figure 12, with the increase of the testing temperature, the thermoelectric merit ZT of the samples increases slightly at the initial stage and then significantly decreases. When the laser power A is at level 3, scanning speed B is at level 2 and scanning interval C is at level 1, the greatest thermoelectric merit ZT reaches to 0.88 at a temperatures of 350 K. This may be mainly attributed to the samples’ high relative density, low thermal conductivity and large Seebeck coefficient, which are achieved in the condition corresponding to the given parameters.
4. Conclusions

With the aim to develop a new rapid prototyping method to fabricate n-type Bi$_2$Te$_3$-based thermoelectric material Bi$_2$Te$_2.08$Se$_0.15$, this paper presents an experimental study on application of an optimal SLS process to this area. High quality E12/Bi$_2$Te$_2.08$Se$_0.15$ composite samples with good internal microstructure are successfully fabricated using SLS approach. The relative density of the sintered composite could reach about 60%, and further upmost to 82.13% after degreasing. Three factors, laser power, scanning speed and scanning interval will affect the relative density, thermal conductivity, electric conductivity and Seebeck coefficient. With respect to the importance and significance of influence, the order of these three factors is laser power as most important, scanning interval next and scanning speed least. The optimum process parameters and the corresponding maximum ZT value were identified using orthogonal experimental analysis. It is found when the laser power is 22 W, scanning speed is 3000 mm s$^{-1}$, scanning interval is 0.26 mm, the powder layer is 0.10 mm and the preheating temperature is 40 °C, the maximum ZT value at 350 K reaches to 0.88.

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