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DILATOMETRIC ANALYSIS OF THE SINTERING BEHAVIOR OF Bi_2Te_3 THERMOELECTRIC POWDERS

The sintering behavior of p-type bismuth telluride powder is investigated by means of dilatometric analysis. The alloy powders, prepared by ball milling of melt-spun ribbons, exhibit refined and flake shape. Differential thermal analysis reveals that the endothermic peak at about 280°C corresponds to the melting of bismuth, and peaks existing between 410°C and 510°C are presumably due to the oxidation and crystallization of the powder. The shrinkage behavior of ball-milled powders was strongly dependent of heating rate by the thermal effect exerted on specimens. In the case of 2°C/min, the peak temperature for the densification is measured at 406°C, while the peak temperature at a heating rate of 20°C/min is approximately 443°C. The relative density of specimen pressureless-sintered at 500°C exhibited relatively low value, and thus further study is required in order to increase the density of sintered body.

Keywords: Bi_2Te_3, Dilatometric analysis, Sintering behavior, Microstructure

1. Introduction

Bi_2Te_3-based alloys have been widely used as thermoelectric materials for thermoelectric generator and cooling around the room temperature [1,2]. These alloys are commercially manufactured by single crystal growth methods such as zone melting and Bridgman techniques, but they have disadvantages of low mechanical strength and large losses of raw materials [3,4]. To overcome this problem, powder metallurgy technique has been applied in the preparation of polycrystalline Bi_2Te_3-based alloys. The conventional pressure-assisted sintering techniques, such as hot pressing, spark plasma sintering and hot isostatic pressing, are helpful to prevent the grain growth and preserve the nanostructures during sintering processes [5,6]. However, these processes can produce only alloy articles of simple geometrical shapes and would be expensive and unsuitable for mass production.

For many potential applications of thermoelectric materials, the pressureless sintering process would be preferable if sufficiently dense pellets with required properties could be achieved [7]. However, there has been reported few details of the pressureless sintering behavior. The first purpose of this study, therefore, is to fabricate p-type Bi_2Te_3-based alloys by pressureless sintering, which subsequently can break through the mass production problem. Further, the densification behavior of thermoelectric powder is investigated by means of dilatometric analysis, which is very useful for studying the sintering kinetics.

2. Experimental

p-type bismuth telluride powder is prepared by high energy ball milling and melt spinning process. The resulting ribbons with a few micrometers thick were ball-milled in a 3D mixer for 5 h using a ball to powder weight of 5:1. The thermal behavior of the ball-milled powders was analyzed with the differential thermal analysis (DTA, DTG-60, Shimadzu) during heating up to 650°C at 10°C/min in N_2 atmosphere. The powders were pelletized into cylinders by pressing at 50 MPa by die compaction method, followed by cold isostatic pressing at 300 MPa in order to minimize the shrinkage anisotropy. The average green density of powder compact was 57.2% of theoretical value.

Sintering behavior was monitored by heating up to 550°C under a N_2 atmosphere using a push-rod type thermomechanical analysis (TMA, Q400, TA instrument) with heating rates of 2, 5, 10 and 20°C/min. The shrinkage in axial direction was measured by linear variable differential transducer under an applied pressure of 0.1 N. Phase identification of the powders was performed

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by X-ray diffraction (XRD, Rigaku Denki Co.) analysis, using Cu K_α radiation. The microstructure of samples was evaluated using field-emission scanning electron microscopy (FE-SEM, JEOL Techniques).

3. Results and discussion

Typical SEM images of the melt-spun ribbons and ball-milled powders are shown in Fig. 1(a) and (b), respectively. The melt spinning process produces flake shape. After ball milling for 5 h, the powders exhibited refined and irregular flake shape with an average particle size of 1.8 μm. DTA result for the ball-milled powder is presented in Fig. 2, where various endothermic and exothermic peaks can be observed. The endothermic peak at about 280°C corresponds to the melting of bismuth, and peaks existing between 410°C and 510°C are presumably due to the oxidation and crystallization of the powder [8,9]. This result indicates that the powder produced by the melt spinning and milling process is considered to contain some metal elements rather than a stable alloy, and further studies are required for detailed analysis.

The XRD profiles registered for the p-type Bi_2Te_3-based alloy are shown in Fig. 3. From the comparison to the powder diffraction file (JCPDS, # 72-1836), in the region of XRD-resolution, the pattern of the powders can be attributed to the $(Bi_{0.225}Sb_{0.775})_2Te_3$ phase. As shown in Fig. 3(a), the ball-milled powder showed a strong (110) preferred orientation. Conversely, the powders heated at 280°C and 600°C exhibited (015) orientation and no particular change in the peak position and intensity. From consideration of DTA result shown in Fig. 2, the change in preferred orientation is believed to be related to the compositional non-uniformity of the raw powder and the microstructure change during heat treatment of the ball-milled powder [10].

Fig. 4 shows the linear sintering shrinkage versus temperature curve for p-type bismuth telluride powder compacts obtained by heating up to 550°C with different heating rates in a N_2 atmosphere. As clearly shown in figure, the shrinkage behavior of ball-milled powders was strongly dependent of heating rate. In order to investigate the shrinkage behavior of

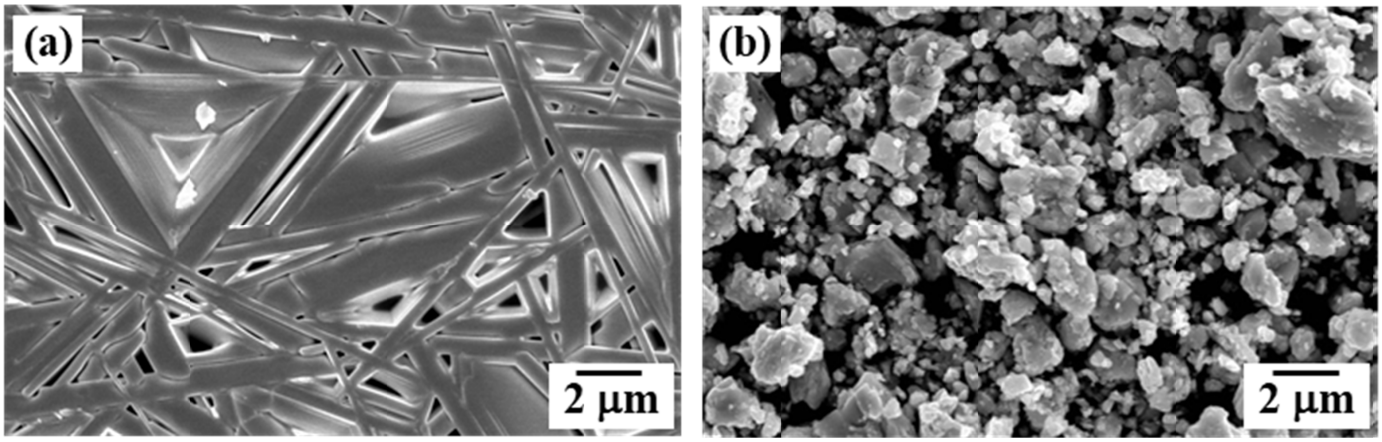

Fig. 1. SEM images of (a) the initial and (b) ball-milled p-type Bi_2Te_3 powder

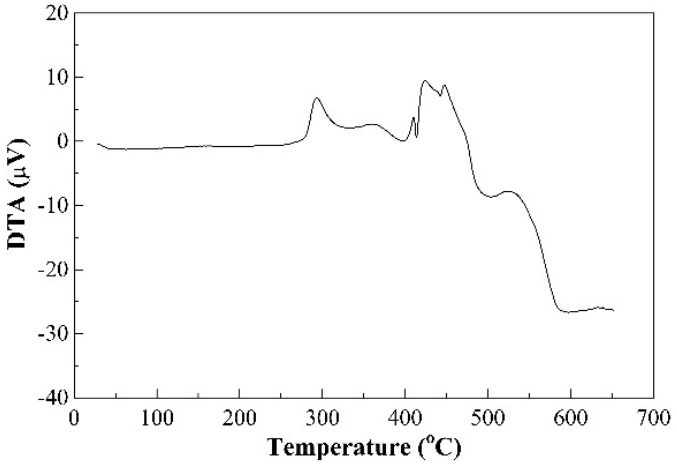

Fig. 2. DTA curve for Bi_2Te_3 powder, obtained at a scanning rate of 10°C/min in N_2 atmosphere

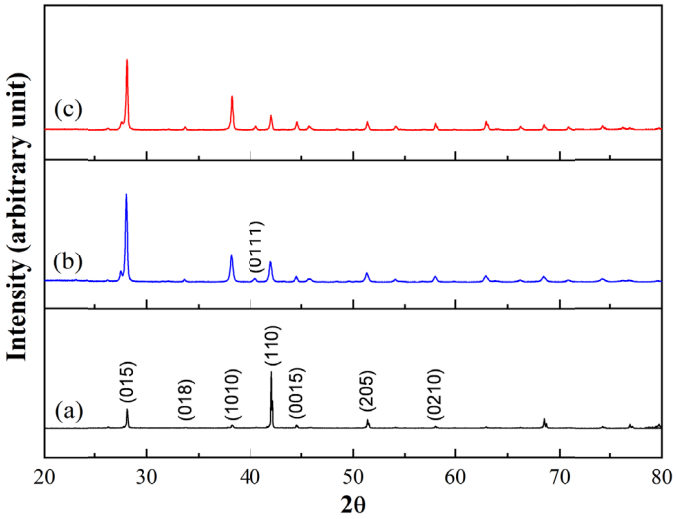

Fig. 3. XRD profiles of the powder at different stages of processing: (a) ball milling, (b) and (c) heat treatment in N_2 atmosphere at 280°C and 600°C

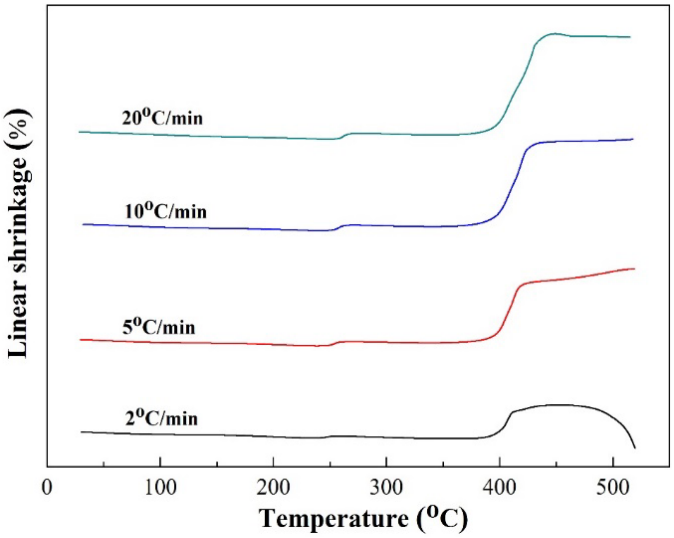

Fig. 4. Change in linear shrinkage of p-type Bi_2Te_3 powder compacts during heating with different heating rates in a N_2 atmosphere

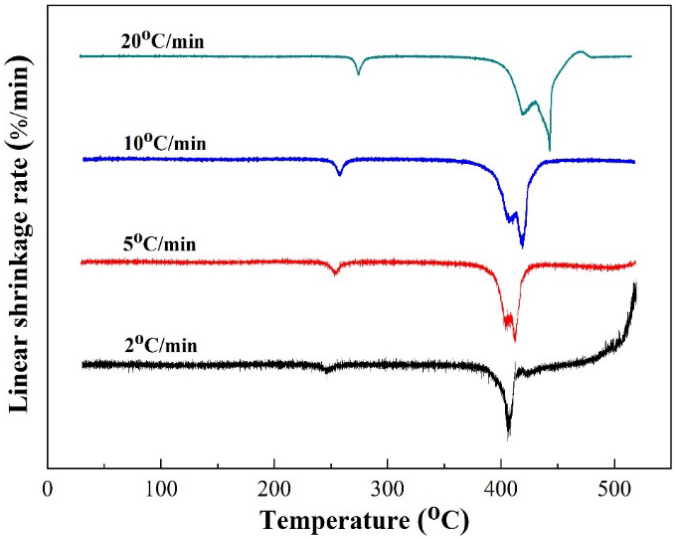

Fig. 5. Change in shrinkage rate as a function of temperature with different heating rates

powder in detail, the linear shrinkage rate, i.e. the first derivative (dY/dt, $Y = dl/l_o$) with respect to time was calculated from the shrinkage-temperature curve.

The plot of linear shrinkage rate (dY/dt) versus temperature with heating rate is shown in Fig. 5, where two different peaks can be observed. The first one at about 250°C is due to the melting of bismuth, as explained in Fig. 2. The second peak temperatures are a different value form the heating rate. In the case of 2°C/min, the peak temperature for the densification is measured at 406°C, while the peak temperature at a heating rate of 20°C/min is approximately 443°C. Such differences in peak temperature can be explained by the thermal effect exerted on specimens, because the powder compact with low heating rate had a longer exposure time during heating than that with higher heating rate. Thus, this result is strongly suggested that temperature above 450°C is required for the sintering of p-type bismuth telluride powder compacts.

In order to compare the microstructural change according to the sintering process, the bismuth telluride powders were densified by pressureless sintering and spark plasma sintering. As shown in Fig. 6, all sintered specimens exhibited flake type grains. The relative density of specimen pressureless-sintered at 500°C exhibited 64.4%, while that after spark plasma sintering at 400°C for 10 min showed a value of 85.9% due to the self-heat generation, activation of the particle surface and high-speed mass transfer [11]. In order to manufacture high-density sintered body by using pressureless sintering, further research is, therefore, needed to analyze the density improvement and resulting thermoelectric properties.

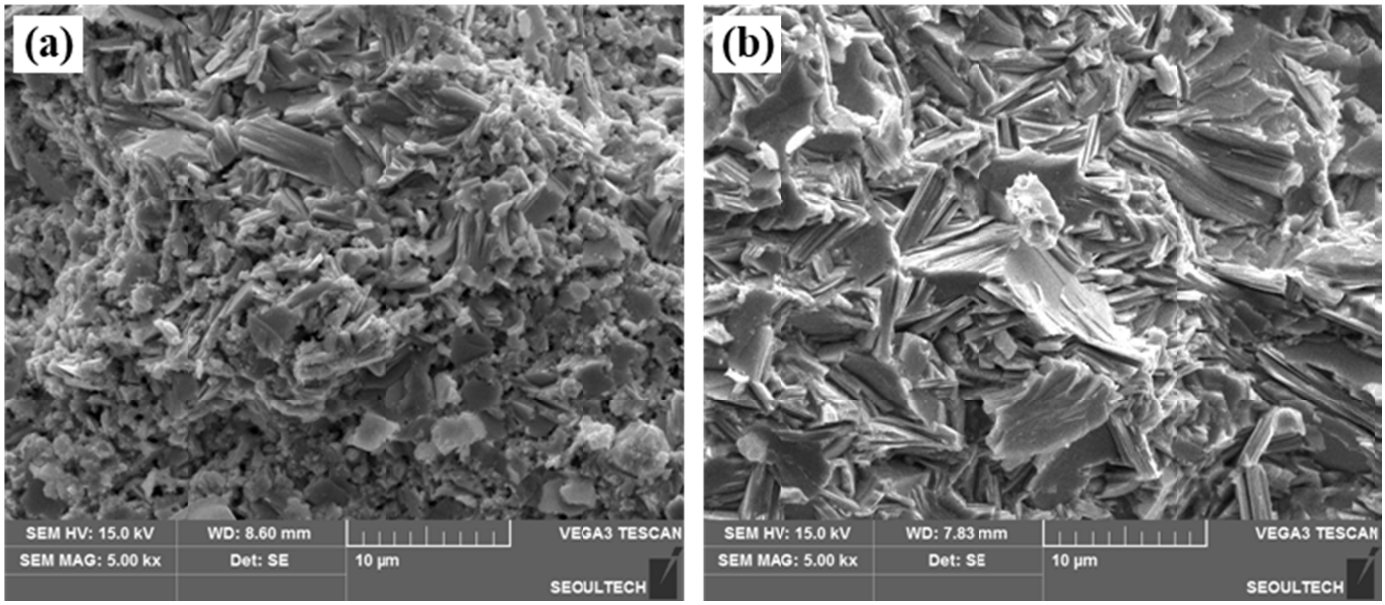

Fig. 6. Fracture surfaces of the of p-type Bi_2Te_3 powders processed by (a) pressureless sintering at 500°C and (b) spark plasma sintering at 400°C for 10 min

4. Conclusions

The densification behavior of p-type bismuth telluride by pressureless sintering, which subsequently can break through the mass production problem, was investigated. The alloy powders, prepared by ball milling of melt-spun ribbons, were pelletized into cylinders by pressing at 50 MPa by die compaction method, followed by cold isostatic pressing at 300 MPa. The DTA curve exhibited various peaks for melting of bismuth, oxidation and crystallization of ball-milled powders. Linear shrinkage analysis revealed that the shrinkage peak temperatures of powder compacts were measured at 406°C and 443°C in the case of 2°C/min and 20°C/min, respectively. The relative density of specimen pressureless-sintered at 500°C exhibited relatively low value, and thus further study is required in order to increase the density of sintered body.

Acknowledgments

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