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学位論文の概要及び要旨

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題　　目　Processing, Microstructure, and Thermoelectric Properties of Bi_2Te_3-based Bulk Materials

(Bi_2Te_3系バルク材料のプロセッシング，組織および熱電性質に関する研究)

学位論文の概要及び要旨

The energy crisis and its attached environmental pollution have become urgent issues on a global scope. Thermoelectric conversion, as one of the most promising ways, has been proposed to face the impending energy shortage and environmental pollution. The conversion efficiency of a thermoelectric device depends strongly on dimensionless figure of merit (ZT) of the materials ($ZT=\alpha^2T/(\rho\kappa)$, where α, ρ, κ, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively).

Bi_2Te_3-based compounds, known as the most effective thermoelectric materials near room temperature, have been widely used in various electronic cooling devices, owing to fast and precise control of temperature and free of noise during the operations. The current fabrication methods of Bi_2Te_3-based compounds mainly include unidirectional solidification and powder metallurgy techniques. The products grown by unidirectional solidification show high thermoelectric performance, but weak mechanical strength limits their applications due to large grain sizes and existence of cleavage planes along the basal plane. On the other hand, although the products fabricated by powder metallurgy exhibit high comprehensive mechanical strength, their thermoelectric performance is not satisfied. Moreover, the thermoelectric performance of Bi_2Te_3-based compounds is much better in the directions parallel to the basal plane than to the *c*-axis. Thus, in the present research, from the viewpoints of grain refinement and preferred orientations, the combination of mechanical alloying (MA) and hot-extrusion was proposed to fabricate Bi_2Te_3-based materials, so as to improve the thermoelectric and mechanical properties simultaneously. The objective of this research was to understand the relationships among processing conditions, microstructure, texture, thermoelectric and mechanical properties.

Sound and dense *p*-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ and *n*-type $Bi_2(Se_{0.05}Te_{0.95})_3$ bulk materials were successfully fabricated by MA and hot-extrusion technique in a temperature range of 340-450^{o}C. The combination of MA and hot extrusion resulted in significant grain refinement and preferential orientation. The (0001) basal planes in the extrudates were preferentially oriented parallel to the extrusion direction. The electrical resistivity and thermal conductivity decreased with increasing extrusion temperature due to grain growth. Small change of the Seebeck coefficient for *p*-type extruded samples measured at room temperature was found, while *n*-type extruded samples showed significant decrease as the extrusion temperature increased. As a result, a maximum value of $ZT = 1.2$ for *p*-type sample extruded at 400°C was obtained, while a lower ZT_{max} value of 0.47 was found for *n*-type sample extruded at 400°C. In addition, all the extruded samples exhibited much higher hardness values than those prepared by conventional techniques.

A Te-rich phase was observed in the extruded samples. The formation of Te-rich phase is attributed to two different mechanisms: sublimation of Te and eutectic reaction. The former occurs at any extrusion temperature and leads to formation of small-sized Te-rich phase, while the latter occurs at ≥400°C and the resultant Te-rich phase possesses large sizes. The small-sized Te-rich phase was distributed discretely around the grain boundaries in extruded samples. The distribution of the Te-rich phase was related to extrusion temperature. The Te-rich phase caused decreases in both grain size and orientation degree. Moreover, the Te-rich phase led to a significant decrease in the Seebeck coefficient and increase in thermal conductivity, respectively, which resulted in a significant reduction in *ZT* value.

Effect of Cu-doping on microstructure and thermoelectric properties was also investigated. Fine-grained microstructures with a submicron order were observed in hot-extruded $Cu_xBi_2Te_{2.85}Se_{0.15}$ (x=0-0.05) samples. With the increase in Cu content, the carrier concentration was decreased, resulting in increases of the Seebeck coefficient and electrical resistivity, as well as decrease of thermal conductivity. The resultant *ZT* value exhibited a significantly increased tendency, and a largest *ZT* value of 0.86 was achieved at room temperature for the $Cu_{0.05}Bi_2Te_{2.85}Se_{0.15}$ sample.

Heat treatment was carried out to reduce the lattice defects induced by mechanical deformation during MA and hot-extrusion processes and thus to improve thermoelectric properties. The effect of annealing on microstructure, thermoelectric and mechanical properties of extruded $(Bi_{0.2}Sb_{0.8})_2$ samples was investigated. With the increase in annealing temperature, the sublimation of Te becomes significant, which leads to a reduction of relative density. Significant effect of annealing on thermoelectric properties was found for the extruded samples. Take the sample extruded at 340°C as an example, significant increase of the Seebeck coefficient and decrease of electrical resistivity were obtained at annealing temperatures of ≤380°C. As a result, evident improvement in *ZT* value was achieved. Moreover, although the Vickers hardness exhibited a decreased tendency with increasing annealing temperature, the hardness values still showed a higher level than that of zone-melted sample.

From a viewpoint of mass production, rapid solidification (RS) such as gas atomization was tried to prepare *p*-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ powder to replace MA, followed by consolidation using either spark plasma sintering (SPS) or hot-extrusion method. All the SPSed samples showed high relative density and fine-grained microstructures. Furthermore, the extruded samples exhibited preferred orientation, and the basal plane was preferentially oriented parallel to the extrusion direction. As sintering temperature increased, the change of carrier concentration was small, while the mobility increased, which resulted in a small variation of the Seebeck coefficient and a decrease in electrical resistivity. A *ZT* value of 1.1 was achieved for the sample SPSed at 400°C. In addition, the samples had high hardness values, although there was a reduction with increasing sintering temperature due to grain growth. Therefore, the combination of RS and hot extrusion is expected to fabricate high performance Bi_2Te_3-based thermoelectric materials, so as to promote their industrial applications and thus contribute to improvement of energy shortage and environmental pollution issues.