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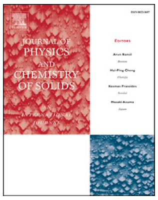

Preparation and optimization of thermoelectric properties of Bi_2Te_3 based alloys using the waste particles as raw materials from the cutting process of the zone melting crystal rods

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ABSTRACT

The p-type Bi_2Te_3 alloys were prepared using the waste particles from the cutting process of the zone melting crystal rods as the main raw materials by impurity removal process including washing, carbon monoxide reduction and vacuum metallurgical process. The thermoelectric properties of the Bi_2Te_3 based bulk materials were optimized by component adjustment, second smelting and resistance pressing sintering (RPS) process. All evidences confirmed that most of impurities from the line cutting process and the oxidation such as Sb_2O_3, Bi_2O_3 and $Bi_2Te_4O_{11}$ could be removed by carbon monoxide reduction and vacuum metallurgical process adopted in this work, and the recycling yield was higher than 97%. Appropriate component adjustment treatment was used to optimize the carrier content and corresponding thermoelectric properties. Lastly, a $Bi_{0.36}Sb_{1.64}Te_3$ bulk was obtained and its power factor (*PF*) could reach 4.24 mW m^{-1} K^{-2} at 300 K and the average *PF* value was over 3.2 mW m^{-1} K^{-2} from 300 K to 470 K, which was equivalent with the thermoelectric performance of the zone melting products from high purity elements Bi, Te and Sb. It was worth mentioning that the recovery process introduced here was a simple, low-cost, high recovery rate and green recycling technology.

1. Introduction

As one of the best thermoelectric materials near room temperature, Bi_2Te_3 based thermoelectric materials are also the most widely studied thermoelectric materials [1–3], and great progress in the fields of bulks [4,5] and thin films [6–8] had been made, especially the zone-melted Bi_2Te_3 based alloys [9,10] have been commercialized for several decades. However, its poor mechanical property is always one of the most serious problems in the refrigeration device manufacturing and application process [11], which results in the low material utilization rate (less than 50%), and generates a large number of waste materials containing about ~48 tons of Te in the semiconductor refrigeration industry every year [11,12]. Meanwhile the thermoelectric waste also contains Bi, Sb, Se, Pb, Ni, Sn and other useful elements. The abundance of Te, Bi and Se in the earth's crust are only 0.001 ppm, 0.025 ppm, 0.05 ppm, respectively, which are even lower than that of Ag (about 0.08 ppm), and the abundance of Sb is only 0.2 ppm, the price of 99.99% Te and 99.99% Se is about five times and two times 99.99% Cu [13]. More important, the Bi, Sb, Te, Pb, Se and their compounds are not only rare and expensive but also toxic and dangerous [13,14].

In general, the hydrometallurgical technology is used to extract the single elements such as Bi, Te, Sb and Se from the thermoelectric waste materials. Now, the traditional hydrometallurgical recycling technology mainly falls into two categories [12]. (1) For the waste materials of high purity such as the head and tail of the zone melting crystal rod and block waste, it is oxidized by adding alkali in the smelting process, and then Te, Bi are separated by hydrometallurgical technology. (2) For the waste materials of low purity such as various chips and cutting powders, they are oxidized by oxidant in hydrochloric acid solution, then Te is retained in the residue, finally Te is obtained by refining the residue. Unfortunately, both of strategies based on the hydrometallurgical technologies have the shortcomings such as multi-step, high cost, long cycle, complicated operation and large environmental load because of wet chemical metallurgy process. So a simple, low-cost, high recovery rate and green recycling technology is urgently needed.

In this paper, the Bi_2Te_3 based waste particles were recycled by

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carbon monoxide reduction [15–17] and vacuum metallurgical [18,19] technology. Elements Se, Pb, Ni, Sn were not separated from the waste particles and they used as the dopants, which would affect the carrier contents and thermoelectric properties of the sample. In our works, excess Sb and Te were added into the samples to counteract the adverse effects of elements Se, Pb, Ni and Sn so as to regulate thermoelectric properties. We calculated the thermodynamic parameters of carbon monoxide reduction and the saturated vapor pressure of bismuth, antimony, tellurium and their oxides, to demonstrate the feasibility of removing impurity (Sb_2O_3, Bi_2O_3 and $Bi_2Te_4O_{11}$) in theory. Furthermore, the Bi_2Te_3 based cutting waste granules were chosen as raw materials to prepare p-type Bi_2Te_3 based thermoelectric materials by washing, carbon monoxide reduction, vacuum metallurgical removing impurity, component adjustment, second smelting and resistance pressing sintering (RPS) process. The thermoelectric properties of the sample from the waste particles were equivalent with the thermoelectric performance of the zone melting products from high purity elements Bi, Te and Sb. The overall recycling technology is a green process with no secondary pollution, low cost and high recovery rate (above 97%).

2. Experiment

In this work, the initial cutting waste granules were obtained from Xianghe Dongfang Electronic Co., LTD (Hebei, China). These cutting waste granules were contaminated by their own oxidations and linear cutting liquid. A typical carbon monoxide reduction and vacuum metallurgical procedure was performed. Firstly, the deionized water and absolute ethyl alcohol were used to remove the contaminants from linear cutting liquid. Then, the waste granules were dried in a vacuum drying oven for 12 h at 383 K, weighed, loaded in a quartz glass tube, and then placed in a vacuum well-like melting furnace. Subsequently, the furnace was heated to 943 K under carbon monoxide reduction atmosphere. The reduction time was 60 min, and the flow rate of carbon monoxide was fixed at 800 ml/min. Then it took another 30 min under vacuum at 943 K, and the degree of vacuum was held at 100 Pa. Lastly, the purified ingot was obtained. In order to obtain the alloys with different nominal stoichiometry ($Bi_xSb_{2-x}Te_3$, $x = 0.36, 0.4, 0.44$), the appropriate amount of high purity (99.99 wt. %) Sb and Te granules were added into the purified ingots. The raw materials were sealed in a quartz glass tube under vacuum and then were melted in a rocking furnace at 983 K for 120 min. Then, the alloys with different nominal stoichiometry were obtained. Subsequently, the alloys were ground into powders with size of ~38 μm. Finally, these powders were sintered by resistance pressing sintering (RPS) process at 723 K for 15 min under an axis pressure of 38 MPa in argon atmosphere and the heating rate was 50 K/min [20,21]. By comparison, the purified ingot without added elements Sb and Te was also ground and sintered in the same condition.

The phase structure of the bulk samples were identified by X-ray diffraction (XRD, Philips) using an X'Per pro diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å). The morphology and composition of bulk samples were analyzed by field-emission scanning electron microscopy (FESEM) (FEI, Nova400 NanoSEM) and energy dispersive X-ray spectroscopy (EDS). The saturated vapor pressure of bismuth, antimony, tellurium and their oxides are calculated by the online software FactSage 7.0. The measured samples were cut into rectangular bars with an approximate dimension of $3 \times 3 \times 15$ mm^3 for testing electrical transport properties. The seebeck coefficient (S) was measured by applying a dynamic temperature gradient (ΔT, 4–8 K) between both ends of the bars and measuring the output voltage (ΔV) between them, and the seebeck coefficient was obtained by calculating the slope of the linear regression line through the least square method. The electrical conductivity (σ) was measured by four terminal methods. The electrical properties of all bulk samples were measured in a direction perpendicular to the press direction during RPS process. The Hall coefficient (R_H) was measured by the van der Pauw method using the Hall-effect measurement system (HMS-5500, Ekopia) under a magnetic field of 0.55 T. The carrier concentration (n) and mobility (μ) were calculated according to the equations: $n = 1/|R_H|e$ and $\mu = \sigma/ne$, where e is electrical charge of electron.

3. Results and discussion

Fig. 1 shows the photos, SEM, the corresponding EDS, and XRD results of the initial waste granules. The surface of waste granules is black and no metallic luster (Fig. 1(a)), indicating that there are impurities (such as oxides) on their surface. The EDS (Fig. 1(c)) and XRD results (Fig. 1(d)) further confirm the presence of Sb_2O_3, Te, Bi_2O_3, $Bi_2Te_4O_{11}$ apart from the main phase of $Bi_xSb_{2-x}Te_3$. Hence, the main impurities of the waste granules are Sb_2O_3, Bi_2O_3 and $Bi_2Te_4O_{11}$.

There are usually two ways to remove oxide without adding new impurities: (1) using H_2 or CO to restore the oxide, resulting in the formation of the gaseous H_2O or CO_2 to leave system [15–17]; (2) volatilization of the oxide under high vacuum based on vacuum metallurgical recycle process [11,18,19]. In this work, carbon monoxide reduction and vacuum metallurgical were used to remove impurity [11,15–19].

Fig. 2 depicts the standard molar reaction Gibbs free energy ($\triangle G^\theta$) of Bi_2O_3, Sb_2O_3, TeO_2 and CO and the logarithm of standard equilibrium constant ($\log K^\theta$) of the reduction reaction for these oxides reduced by CO at different temperatures. It can be found that the value of the standard molar reaction Gibbs free energy ($\triangle G^\theta$) of Sb_2O_3, Bi_2O_3, TeO_2 are all negative. It means that the oxide reaction of Sb, Bi, Te can be carried spontaneously. In addition, the $\triangle G^\theta$ of Sb_2O_3 and Bi_2O_3 is much lower than that of TeO_2, suggesting that the oxide reaction of Sb, Bi is easier than that of Te, which may be the reason that there are no TeO_2 in the initial waste granules. According to Professor Ma et al., when logarithm of standard equilibrium constant ($\log K^\theta$) is greater than 5, the reaction is an irreversible reaction; and when the $\log K^\theta$ is less than 5, the reaction is a reversible reaction [22]. In our works, when the $\log K^\theta$ is 5, it represents the dashed line in Fig. 2 (b). The K^θ of the reduction reactions between Bi_2O_3 (or TeO_2) and CO is greater than 5, and it is an irreversible reaction and will preferentially take place. Unfortunately, the $\log K^\theta$ of the reduction reaction between Sb_2O_3 and CO is less than 5, and it is a reversible reaction and reaction is very slower. So Bi_2O_3 and TeO_2 can be easily reduced by CO, but Sb_2O_3 can't [23]. The corresponding contents were added in the revised manuscript. According to the above analysis, the impurities of Bi_2O_3 and $Bi_2Te_4O_{11}$ in the initial waste granules are easy to be reduced by CO, but Sb_2O_3 is difficult to remove by means of reduction.

Fig. 3 depicts the saturated vapor pressure of Sb, Bi, Te and Sb_2O_3 [18,19]. It can be found that the saturated vapor pressures of Sb_2O_3 and Te are much larger than those of Sb and Bi, suggesting that Sb_2O_3 and Te are more easily volatile, and the Sb_2O_3 can be removed by the vacuum metallurgical method. Taking into account the effect of melting temperature ($BiSbTe_3$ and Sb_2O_3) and saturated vapor pressures of Sb_2O_3 and Te, the temperature of vacuum metallurgical is identified at 943 K. As shown in Fig. 3(a), the saturated vapor pressures of Sb_2O_3 and Te are 1.06 kPa and 1.34 kPa at 943 K, but the saturated vapor pressure of Sb and Bi are very low, and Sb and Bi are not easy to volatilize under vacuum.

Fig. 4 shows the real photo of quartz tube after vacuum melting and carbon monoxide reduction process, SEM and the corresponding EDS results of the two areas of A and C on the inner wall of quartz tube. It can be found that the quartz tube is obviously divided into three areas: pale yellow area (A), white area (B) and gray area (C). As shown in Fig. 4(a), when the temperature of smelting sample is 943 K, the temperature of area A (pale yellow area) and area C (gray area) are about 781 K and 647 K, respectively, which are determined by thermocouples. From the result of EDS, it can be confirmed that there are elements O and Sb in the areas A and elements O, Si, Te and traced Sb in the area of C, and no impurities fall into the white area of B. There is silicon in the area C and no silicon in the area A due to different sampling methods for the EDS analysis. There are large amount of volatile substance in the area A, and can be removed directly from the quartz tube for the EDS analysis. So