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The exploration for synthesizing $CoSb_3$ powder by mechanical alloying

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Abstract

In order to explore new technologies to synthesize the $CoSb_3$ type thermoelectric materials, the basic technologies of preparing $CoSb_3$ powder by mechanical alloying were investigated. The phase transformations and crystal size of Co–3Sb powder were analyzed by X-ray diffraction (XRD). The shape and grain size of $CoSb_3$ powder were observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The results show that the single phase $CoSb_3$ powder with 20–35 nm nanocrystalline was prepared successfully by milling for 5 h under a ball to powder ratio of 20:1 and a working voltage of 110 V for the high-energy mill. It is considered that $CoSb_3$ is a metastable phase in long time high-energy milling, as it tends to decompose.

Keywords: $CoSb_3$; Mechanical alloying; Thermoelectric materials; Skutterudite

1. Introduction

The performance of thermoelectric materials is characterized by the dimensionless parameter of merit,

$$ZT = \left(\frac{\alpha^2\sigma}{\kappa}\right) T,$$

where T is the temperature, α is the Seebeck coefficient (or named as thermoelectric power), σ and κ refer to the electric and thermal conductivity, respectively. A satisfactory thermoelectric material is required to demonstrate low κ, high α and σ, and thus a high ZT value which simply indicates high thermoelectric conversion efficiency. The $CoSb_3$ type thermoelectric material can be used to generate electricity at medium temperature, and it is considered as one of the most promising thermoelectric materials because of many excellences [1–4]. First, it has complex skutterudite structure, as shown in Fig. 1 [2], which leads to a large Seebeck coefficient. Second, it can be made into P and N type materials by doping or substituting with other elements, such as $M_yCo_{4-y}Sb_{12}$ (M = Fe, Ni etc. metal elements) or $RE_xM_yCo_{4-y}Sb_{12}$ (RE-lanthanon or other elements) filled with proper elements in skutterudite void. These methods can improve effectively thermoelectric properties. However, the physical properties of Co, Sb, Fe and Ni shown in Table 1 are very different. Especially, Sb element volatilizes dramatically when melted due to its low melting point. Therefore it is difficult to prepare $CoSb_3$ type thermoelectric materials with stoichiometric proportion. For extensive application of $CoSb_3$ type thermoelectric materials, it is necessary to develop novel non-melting preparing technologies.

Mechanical alloying (MA) has been an important developed technology for preparing novel materials for about 40 years. It is a process that enables mixed metal or nonmetal powders to be alloyed and crystallized or made into amorphous materials by repeated extrusion and deformation, fracture and impacting, cold welding and interdiffusing in high-energy milling. Owning to the mechanism of solid reaction, MA is not governed by the factors as vapor pressure and melting points of raw materials. So it makes possible to synthesize some materials almost unattainable by conventional melting technologies and some quasi-stable and unstable novel materials that are far away from thermodynamic equilibrium [5–8]. Thus MA has drawn more attentions in the research and preparation of amorphous, quasi-crystal and nanocrystalline materials. The phase structure changes of the Co–Sb powder and synthesizing technologies of $CoSb_3$ alloy powder were investigated in this work.

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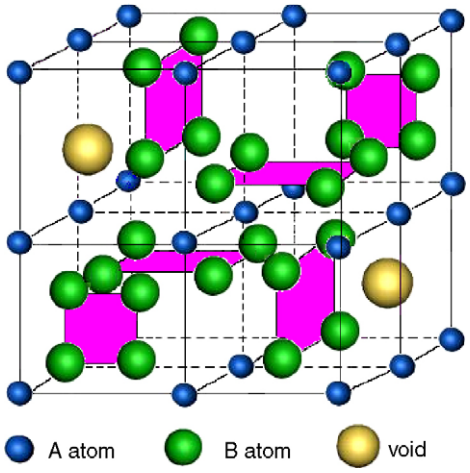

Fig. 1. Schematic of the skutterudite structure.

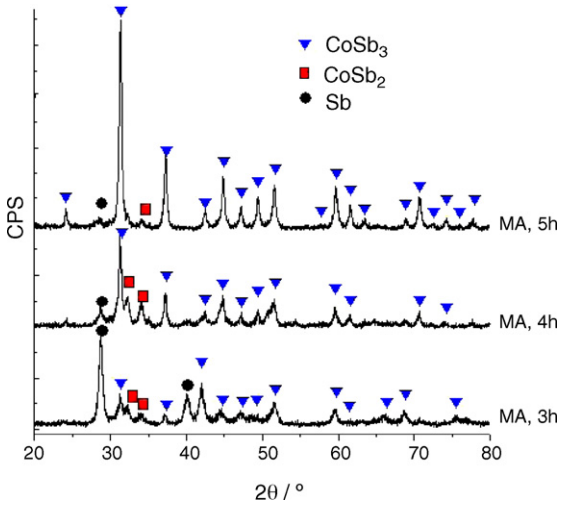

Fig. 2. The phase changes of Co–Sb powder milled for 3 h, 4 h and 5 h.

Table 1
The physical properties of several elements

Element	Co	Sb	Fe	Ni
Melting point (°C)	1495	630.5	1536.5	1453
Boiling point (°C)	2900	1380	3000	2730
Lattice type	Hexagon	Rhombus	bcc	fcc

2. Experimental

The raw material powders of cobalt (purity > 99.5%, average granularity was 40.0 μm) and antimony (purity > 99.5%, average granularity was 200–500 μm) were blended in the stoichiometric ratio of $CoSb_3$. Mechanical alloying process was performed in a GN-II type high-energy ball mill manufactured by Shenyang New Electronmechanical Equipment Factory of China. The working voltage of the ball mill was 110 V to power the rotating velocity of 1100 rpm with a working current about 1.5 Å. Steel balls with different diameters (φ 4–15 mm in a certain proportion) were encased into ball pot with Ar gas to prevent the powders from being oxidized in milling process. The phase changing and crystal size of the Co–Sb powders were analyzed by X-ray diffraction (XRD) on a D/max-3c model (Japan Rigaku) XRD system with Ni-filtered Cu Ka radiation ($\lambda = 1.5059$ Å) with steps of 0.02°. The morphology of the $CoSb_3$ powder was observed with scanning electron microscope (SEM, JEOL X-650) and transmission electron microscope (TEM, H-800).

3. Results and discussion

3.1. $CoSb_3$ powder synthesized by mechanical alloying

Fig. 2 shows the XRD patterns of the Co–Sb binary powders milled for different time with a steel ball to powder ratio of 20:1. There are many diffraction peaks for $CoSb_3$ phase and evident peaks for minor $CoSb_2$ phase in the substances milled for 3 h, but at this time the highest peak at the 2θ angle of 28.75° still pertains to Sb element. However, when milled for 4 h, the Sb peak at 28.75° turns lower obviously, and the highest peak shifts to one at 31.26° that belongs to the $CoSb_3$ phase. The peaks of the minor $CoSb_2$ phase experience no obvious variations. When milled for 5 h, the substance can be considered as single phase – $CoSb_3$ alloy powder, as the peaks of minor phases such as $CoSb_2$ are difficult to be detected from XRD patterns. Here the granularity of the $CoSb_3$ powder distributes unevenly in a range of 2–30 μm measured by the laser particle size analyzer. While the average crystal grain size of the $CoSb_3$ powder falls within 20–35 nm according to the XRD results of several samples and Scherrer formula [9]. Crystal grains in nanometer size can be observed with SEM and TEM, as shown in Figs. 3 and 4. Moreover, there are much finer grains with diameters less than 100 nm in the assembly.

It has been reported that a single phase of $CoSb_3$ cannot be directly obtained by mechanical alloying of the mixed powders. However, the as-mechanical alloyed powders can be easily transformed into single phase $CoSb_3$ following an isothermal heat treatment at 700 °C [10,11]. This is very different from the aforementioned results in this work, because the experimental conditions are different in respect to mill type, milling time, the speed of the mill, and the ratio of ball to powder, etc.

3.2. The phase changes of the $CoSb_3$ powder in further long time milling

Fig. 5 shows the XRD patterns of $CoSb_3$ powders aforetested following longer time milling. The peaks for $CoSb_2$

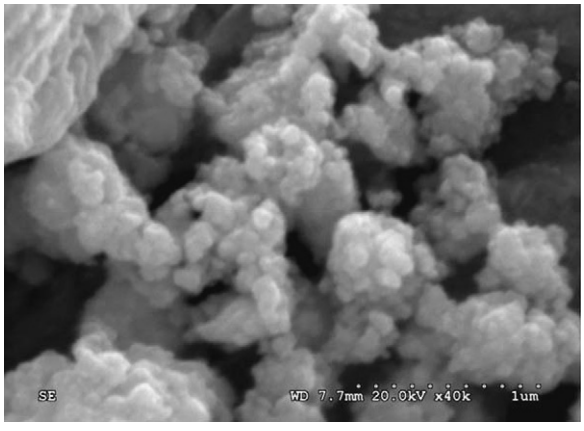

Fig. 3. The morphology of the $CoSb_3$ powder. Steel ball:powder = 20:1; milling time, 5 h.