Journal of Alloys and Compounds 509 (2011) 1722–1728

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Microstructural behavior of the heat treated n-type 95% Bi_2Te_3–5% Bi_2Se_3 gas atomized thermoelectric powders

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ARTICLE INFO

Article history:
Received 11 June 2010
Received in revised form 2 October 2010
Accepted 6 October 2010
Available online 16 October 2010

Keywords:
Thermoelectric material
Powder metallurgy
Gas atomization
Heat treatment
Microstructure

ABSTRACT

In this research, n-type 95% Bi_2Te_3–5% Bi_2Se_3 doped with 0.04% SbI_3 thermoelectric powders were manufactured by gas atomization process and subsequently, the effects of rapid solidification and heat treatment on the microstructure of the powder particles were investigated. The crystal structures were analyzed by X-ray diffraction (XRD) and cross-sectional microstructures were observed by the scanning electron microscopy (SEM). The rapidly solidified powders consist of homogeneously distributed needle shape intermetallic compounds. However, the size of the intermetallic compounds increased with the increasing powder size, whereas the oxygen content in the produced powder decreased. Heat treatment of the powders for various temperatures and periods showed a significant increase in the grain size resulting in a reduction in hardness. In addition, with the increasing heat treatment temperatures and periods, the orientation factor of the powder particles decreased, which is also evident in case of the reduction treated powders.

1. Introduction

The exclusive advantages of thermoelectric cooling module such as small size and weight, spot cooling system, no moving parts and noise, precise temperature control and environment friendly etc. compared with the mechanically operated refrigeration systems [1] have recently drawn a considerable attention in this research field among the scientists and researchers all over the world. Due to good figure-of-merit operating at the region of room temperature, Bi_2Te_3 and its related ternary alloys [2], such as consisting of Bi_2Te_3 with either Bi_2Se_3 or Sb_2Te_3, are the leading thermoelectric materials have long been used for thermoelectric cooling. The crystal structure of Bi_2Te_3 is rhombohedral [3] and shows anisotropic properties [4]. These materials can be prepared by a number of ways, like directionally grown single crystals [5], powder metallurgy techniques [6] and thin films technology [7]. Although directionally grown single crystals are more favorable to use commercially as they exhibit the highest figure of merit [5], the poor mechanical properties due to coarse grain size and easily occurring fractures along the Te(1)–Te(1) cleavage planes, account for material wastage to some extent during the fabrication process of the modules, accompanied by a decrease in the reliability level of the modules during practical applications. On the other hand, fabrication of materials through powder metallurgy technique provides higher compressive strength as well as simultaneous increase in the figure of merit [6] as a result of grain refinements and reduction in lattice thermal conductivity. The required powder can be produced by gas atomization [6], mechanical alloying [8], chemical reactions [9] as well as some other special methods depending on the material, economy and their applications. Among all of these, the gas atomization became attractive due to its efficient and high performance application, easy process control, mass production rate and homogeneous productivity without segregation relative to other manufacturing processes. In powder metallurgy system, materials in the form of powders are usually compacted through extrusion [6], hot pressing [8], spark plasma sintering (SPS) [10] and plasma activated sintering (PAS) [11] to acquire fine microstructures with unique properties. These consolidation processes involve high temperature applications affecting the microstructure of the bulks, and thus altering mechanical and thermoelectric properties. As the mechanical and thermoelectric properties are largely dependent on the microstructures, and the microstructure formation is influenced by the hot consolidation processes, therefore it is an urgent need to analyze and establish the relationships between the material processing parameters, microstructures and their properties, facilitating a full control over the processes in terms of properties. Accordingly, investigation of the heat treated powders can be considered as a pre-requisite and inevitable step that should be accomplished prior to the processing's, in order to understand microstructural behavior of the powders subjected to high temperatures during consolidation processes. Despite a lot of researches were conducted previously on Bi_2Te_3 powders produced by gas

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doi:10.1016/j.jallcom.2010.10.021

atomization and/or milling processes, however, none of those elaborately reported powder characterization and its property variation depending on the heat treatment temperatures as well as the holding time. Hence, the essence of this research represents microstructural investigation of 95% Bi_2Te_3–5% Bi_2Se_3 doped with 0.04% SbI_3 gas atomized powders as a function of various heat treatment conditions.

2. Experimental procedure

High purity (>99.999%) elementary Bi, Te and Se granules were weighed for the required stoichiometric composition of 95% Bi_2Te_3–5% Bi_2Se_3 doped with 0.04% SbI_3 alloy, and placed at a high density graphite crucible in an induction furnace evacuating at 4.4 mTorr. The alloy was melted and superheated 200 °C above the liquidus temperature under Ar atmosphere to make the master alloy, and then bottom pouring the melt through a boron nitride melt delivery nozzle of 8 mm diameter to a N_2 gas operated atomizer working at a pressure of 1.2 MPa, the rapidly solidified powders were produced. The size distribution of the as-atomized powders was carried out by laser diffraction technique using Mastersizer 2000 particle size analyzer. To examine the effect of rapid solidification on the microstructure of the powders, the conventional mechanical sieving method was employed to classify the as atomized powders into small (~45 μm), medium (75–106 μm) and large (180–250 μm) size range. The oxygen content of the powders was determined by the equipment of Eltra ONH-2000 Oxygen/Nitrogen/Hydrogen determinator. In order to understand the effect of high temperature on the microstructures, powders of 65–80 μm size range were heat treated at 300, 350, 400 and 500 °C temperatures for 1, 3 and 5 h. The as atomized powders were also reduced at 360 °C for 4 h under 10% H_2 atmosphere. Crystal structures of the as-atomized, reduction treated and heat treated powders were characterized by X-ray diffractometer (XRD) using high energy monochromatic CuKα radiation (15.418 nm) in the 2θ range from 10 to 70° at a scan rate of 0.05°/s. The morphology and cross-sectional microstructure of the powders were observed by the scanning electron microscopy (SEM) after polishing and etching by a solution of HNO_3 and H_2O in the ratio of 1:1 for 5 s. Vickers hardness of the powder was measured by the Vickers hardness tester applying the load of 98.07×10^{-3} N for 15 s, and the values were averaged.

3. Results and discussion

Fig. 1 represents SEM micrograph showing typical morphology of 95% Bi_2Te_3–5% Bi_2Se_3 doped with 0.04% SbI_3 gas atomized powders in different size range. All the small (~45 μm), medium (75–106 μm) and large (180–250 μm) size powder particles were spherical in shape. It is much desirable to obtain such kind of particles as shown in Fig. 1, since spherical powders with smooth surfaces and fewer satellites contribute to higher packing density and free flowing characteristics. The log normal and cumulative size distribution of the gas atomized powders are illustrated in Fig. 2(a) and (b). A broad and bimodal size distribution of the powders could be observed in Fig. 2(a). The surface weighted mean and volume weighted mean of the particles were 14.13 μm and 68.431 μm, respectively. Generally, gas atomization process results in a wide range of particle size due to variation in the cooling rate, which is inversely proportional to the size of the liquid droplets. Furthermore, bimodal size range of the powders improves the packing density comparing to the monosized powders [12] during the compaction processes, as the smaller particles can easily place themselves at the interstitial positions of the gaps between the larger particles, and thus reducing the voids within the powder particles provides a significant increase in the final density. The cumulative size distribution in Fig. 2(b) indicates D_{10} = 7.291 μm, D_{50} = 22.252 μm and D_{90} = 220.03 μm corresponding to the particle sizes at 10%, 50% and 90%, respectively. The standard deviation was calculated using the equation, $\sigma = \ln(D_{84}/D_{50})$ and found to be 1.91 μm. That means 68% powders fall between 20.34 μm and 24.16 μm, whereas 95% powders have a size range between 18.43 μm and 26.07 μm on volume basis. Since, the thermoelectric and mechanical properties of the bulk depend on the microstructure, and the microstructure is affected by the initial powder size, therefore, the demand of narrow size distribution of powders is gradually increasing. It is expected that an improvement in the design parameters and process parameters of gas atomization would deliver high quality powders, significantly reducing the volume median diameter D_{50} to the finer particle sizes.

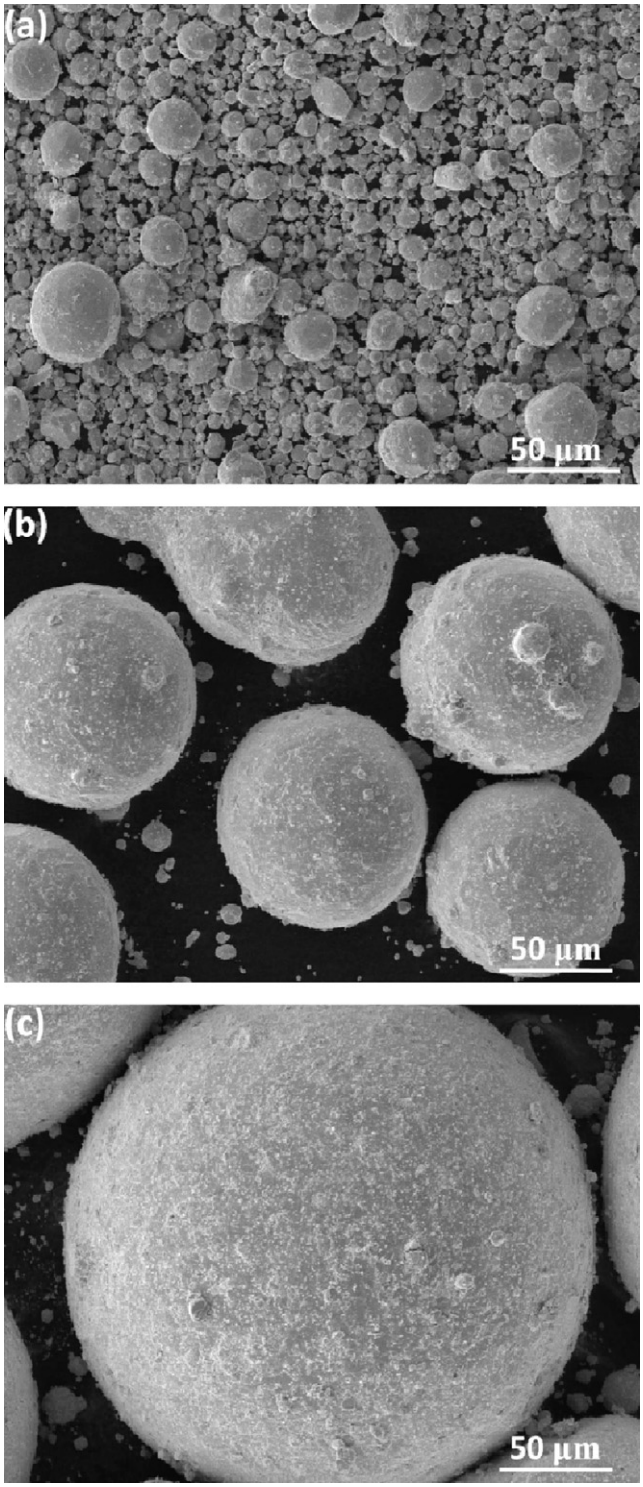

Fig. 1. Morphology of the gas atomized 95% Bi_2Te_3–5% Bi_2Se_3 powders (a) ~45 μm (b) 75–106 μm and (c) 180–250 μm.

The powder fabrication procedure often contaminates the powder by adsorbing oxygen as a film on its surface. Fig. 3 demonstrates the oxygen content of 95% Bi_2Te_3–5% Bi_2Se_3 gas atomized powders according to different size range. It appears that the maximum oxygen content of 240.60 ppm was obtained in the small size (~45 μm) powders due to its high specific surface area. However, with the increasing powder size to medium (75–106 μm)