New technologies for obtaining thermoelectric materials

L D Ivanova, Yu V Granatkina, A G Malchev and I Yu Nikhezina

Baikov Institute of metallurgy and material sciences of the Russian Academy of Sciences (IMET RAS), 119334, Moscow, Russia

E-mail: ivanova@imet.ac.ru

Abstract. New technologies have been developed for production of thermoelectric materials based on fast melt crystallization rates on a cooled rotating disk (melt spinning) and on fast melt solidification in a liquid using the example of bismuth and antimony chalcogenides solid solutions. The use of the developed technologies allows to prepared materials with high strength and thermoelectric characteristics, which significantly exceed the characteristics of materials obtained by traditional methods.

1. Introduction

In this paper, we consider two preparation technologies of particles of thermoelectric materials by rapid crystallization of the melt: melt spinning and melt crystallization in a liquid, which we used to obtain and study the properties of thermoelectric materials based on solid solutions of bismuth and antimony chalcogenides [1-8]. With such methods, when the melt cooling rate reaches $10^4$-$10^6$ K/s during the crystallization of the solid solution, it is possible to suppress the segregation process and the transition of the liquid phase to the solid phase of the same composition. The large overcooling of the melt and the intense heat removal from the crystallization front cause high chemical homogeneity and the acquisition of new mechanical and electrical properties that differ from the properties of materials obtained by alloying in ampoules or directional crystallization methods.

The purpose of this study, on the example of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ solid solution, which used to fabricate the $p$-legs of thermoelectric devices operating in the temperature range of 200-500 K, is to evaluate the advantages of methods for producing particles of the material by melt spinning and melt cooling in a liquid and compare with such material obtaining by fusion in quartz ampoules.

2. Experimental technique

One method of the formation of fine particles, from which compact materials are then formed, is rapid melt quenching on a cooling rotating disc (melt spinning). The scheme of this method of obtaining material is shown in figure 1.

The installation consists of a vacuum chamber 1 made of stainless steel, an airlock compartment 2, a guide sleeve 3 and a compartment for collecting material 4. A DC motor 6 with a cooler 5 on the axis is installed on the bracket inside the chamber. The working surface of the cooler, which is a hollow disk with an outer diameter of 190 mm, a width of 60 mm and a mass of 5 kg, is polished and coated with electroplated chrome to prevent melt sticking. The airlock compartment is designed to install and fix the ampoule 7 with the source material 8, as well as for supplying the gas that pushes the melt through the flange 11. The ampoule is made of a quartz tube with an outer diameter of 34 mm and a wall thickness of 2.5 mm. In the conical part of the ampoule there is an outlet. The ampoule is
fixed in the bracket 9, allowing it to move along the axis and adjust the distance from the outlet to the surface of the disk, which is installed using calibrated metal plates of various thicknesses. The ampoule together with the starting material is placed inside the inductor 10, which is designed to heat the material with high frequency currents. The compartment for collecting material is a steel bowl connected through a vacuum rubber gasket to the guide sleeve. Air is pumped out of the chamber by a fore pump. High purity argon is used as an ejector gas.

Another way to rapid melt crystallization is to quench a melt in a liquid. Figure 2 presents inductive granulating machine (a) and schematic of the cell (b) of the machine used to produce granules though rapid melt solidification in a liquid.

Figure 1. Camera circuit device for melt spinning: 1 — vacuum chamber; 2 — airlock; 3 — guide sleeve; 4 — compartment for collecting material; 5 — cooling disk; 6 — electric motor; 7 — quartz ampoule; 8 — source material; 9 — bracket; 10 — inductor; 11 — ejector gas supply flange; 12 — valve of the vacuum system; 13 — valve for supplying argon to the ampoule; 14 — valve for filling argon into the chamber.

Figure 2. Inductive granulating machine (a) and schematic of the cell (b) of the machine: 1 — graphite crucible; 2 — graphite rod; 3 — thermoelectric material, 4 — inductor, 5 — cooled liquid.

The initial components of thermoelectric materials in a given stoichiometric composition are loaded into a graphite crucible just before the process of melt crystallization, and not synthesized
previously in quartz ampoules, which is one of the distinguishing features of this method. The main condition for rapid cooling is maximum thinning of the jet or portion of the melt just before cooling or at the time of cooling. The melt enters the liquid at a speed of \( \sim 5 \text{ m/s} \), while the cooling rate of the melt could reach \( 10^5 \text{ K/s} \). The change in the rate of crystallization of the melt was carried out by using liquids (water, ethanol, liquid nitrogen), into which the melt flows, cooled to different temperatures (from room temperature to liquid nitrogen temperature).

These two methods were used to obtain particles of the \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \) solid solution, which is used to obtain the \( p \)-branches of thermoelectric devices. Hot-pressed and extruded samples were prepared from these particles, ground in a planetary mill. The morphology of the powders and the cleaved surface of the samples and their microstructure were studied using optical and scanning electron microscopy (SEM). Thermoelectric properties of samples: the Seebeck coefficient \( \alpha \), specific electrical conductivity \( \sigma \), and thermal conductivity \( \kappa \) were measured at room temperature and in the range of 100-600 K. The thermoelectric figure of merit of the samples was calculated \( ZT = \frac{\alpha^2 \sigma T}{\kappa} \) where \( T \) is the temperature.

### 3. Results and discussions

Figures 3 shows SEM images of particles obtained by melt spinning and melt crystallization.

When the melt is spinning (figure 3a-c), the particles have the form of plates, which consist of thin scales that are located with their flat side perpendicular to the cooled surface of the disk. The scales are several hundreds on nanometers in thickness and of several micrometers in length. During the rapid crystallization of the melt in the cooled liquid, the shapes and sizes of the granules depend on the crystallization temperature. Also figure 3 shows SEM images of granules obtained by melt crystallization in liquid nitrogen (d), in ethanol cooled with liquid nitrogen (e) and in water (f). The crystallization temperatures are 100, 180, and 300 K respectively.

The SEM images of the cleavage surfaces and the microstructure of the surfaces of the samples obtained on a metallographic optical microscope after etching polishing sections in a solution \( \text{H}_2\text{O}:\text{HNO}_3 = 1:1 \) during the course of 10 s are shown in figure 4.

![Figure 3](image)

**Figure 3.** SEM images of particles received by melt spinning (a-c) and granules prepared through melt crystallization in liquid nitrogen (d), ethanol cooled with liquid nitrogen (e), and water (f).
Figure 4. SEM images of the cleavage surfaces of a hot-pressed sample from particles obtained by spinning (a) and hot-pressed (b) and extruded (c) samples from granules prepared by melt crystallization in water, and a microstructure image (d) on an optical microscope. A — eutectic based on tellurium.

Hot-pressed samples form particles prepared by melt spinning and hot-pressed and extruded samples obtained from granules crushed in a planetary mill had a fine-crystalline layer structure, the grain sizes in the samples did not exceed a few micrometers (figure 4). All samples contained a small amount of the second phase (tellurium-based eutectic), which can be seen in the form on light inclusions on the microstructures obtained with an optical microscope (figure 4d).

Table 1. 300 K thermoelectric properties of the samples prepared by hot-pressing (1) and by extruding (2) granules ground in a ball mill received by melt crystallization and samples prepared by hot-pressing of particles received by melt spinning (3, 4)

| Samples | T$_{cr}$, K | Preparation method of the samples | $\alpha$, $\mu$V/K | $\sigma$, S/cm | $k \times 10^3$, W/cm K | $k_l \times 10^3$, W/cm K | $ZT$ |
|---------|------------|----------------------------------|-------------------|---------------|-------------------------|-------------------------|------|
| 1       | 300        | hot pressing                      | 203               | 925           | 10.1                    | 5.7                     | 1.1  |
| 2       | 300        | hot extrusion                     | 221               | 862           | 10.8                    | 6.5                     | 1.2  |
| 3       | spin       | hot pressing                      | 230               | 617           | 9.1                     | 6.2                     | 1.1  |
| 4       | spin       | hot pressing                      | 238               | 577           | 9.0                     | 6.3                     | 1.1  |

Thermoelectric characteristics: Seebeck coefficient, electrical conductivity, total and lattice thermal conductivity, thermoelectric figure of merit at room temperature of the samples obtained by different methods are presented in the Table 1.

The samples had a Seebeck coefficient from 203 to 238 $\mu$V/K, an electrical conductivity from 925 to 577 S/cm, a thermal conductivity from 10.8 $\times 10^{-3}$ to 9 $\times 10^{-3}$ W/cm K, and the values of $ZT$ for these samples were 1.15 $\pm$ 0.05 at 300 K. Figure 5 shows the temperature dependences in the range of 100-600 K thermoelectric properties of hot-pressed and extruded samples from powders obtained by crystallization of the melt in a liquid and melt spinning, the thermoelectric properties of which at 300 K are given in the Table. The electrical conductivity of the samples decreases with increasing temperature. The thermal conductivity of the samples begins to increase above 350 K. The temperature dependences of the Seebeck coefficient and the dependences of the thermoelectric figure of merit $ZT$ are curves with a maximum at temperatures of 340-370 K. Such a character of dependencies is typical of degenerate semiconductors. Calculations showed that $ZT_{max} = 1.3 \pm 0.05$ for extruded (2) and hot-pressed (1) samples from granules obtained by melt crystallization in water at 300 K and for hot-pressed sample (4) from particles obtained by melt spinning.
Figure 5. Temperature dependences of the Seebeck coefficient $\alpha$, electrical conductivity $\sigma$, total thermal conductivity $k$, and thermoelectric efficiency $ZT$ of the samples prepared by melt crystallization in a liquid and melt spinning powders. The curve numbers correspond to the sample numbers of the samples in the Table.
4. Conclusions
Two methods for obtaining powders of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ solid solution by rapid melt crystallization are considered: melt spinning and melt crystallization in a liquid. The maximum thermoelectric figure of merit $ZT_{\text{max}} \approx 1.3$ at 350 K was obtained for hot-pressed materials from powder prepared by spinning the melt and from hot-pressed and extruded materials from granules obtained by crystallization of the melt into water and crushed in a planetary mill. Such thermoelectric figure of merit by ~20% exceeds the quality of materials obtained from ingots fused in ampoules with subsequent directional solidification. It has been established that hot-pressed and extruded materials have similar thermoelectric figure of merit.

Advantages of the developed technologies:
- it is possible not to conduct preliminary melting of the initial components in quartz ampoules;
- the composition of the obtained solid solution particles is close to stoichiometry and corresponds to the composition of the initial load;
- it is not necessary to grind for pressing the particles obtained by spinning the melt.

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