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Investigation of the nozzle diameter as a control parameter of the properties of melt-spun $\text{Sb}_{2-x}\text{Bi}_x\text{Te}_3$

V. Ohorodniichuk^{1,2}, A. Dauscher¹, Ph. Masschelein¹, C. Candolfi¹, Ph. Baranek², P. Dalicieux²,

B. Lenoir¹

¹ Institut Jean Lamour, CNRS – Université de Lorraine, Parc de Saurupt, F-54011 NANCY Cedex, France

² EDF R&D, Site des Renardières, Avenue des Renardières – Ecuelles 77818 Moret-sur-Loing Cedex, France

E-mail of corresponding author: viktorija.ohorodniichuk@univ-lorraine.fr

Telephone of corresponding author: + (33) 03 83 58 41 76

Three kinds of $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ samples were prepared by the melt-spinning technique using quartz tubes with different nozzle's diameters (1.0, 0.7 and 0.5 mm) to study the sensitivity of the thermoelectric properties to the variations of this parameter. The melt-spun ribbons were densified by Spark Plasma Sintering (SPS). The melt-spun samples were characterized by powder X-ray diffraction and scanning electron microscopy. The dimensionless figures of merit (ZT) were calculated from the data obtained by measuring the Seebeck coefficient, electrical resistivity and thermal conductivity in the direction perpendicular to the uniaxial pressing direction of SPS. All ZT values for this set of samples were close to 1.0 around 380 K. The highest ZT value was obtained for the sample prepared using the largest nozzle diameter of 1.0 mm. Despite some variations in the carrier concentrations of the samples were observed, these results indicate a weak sensitivity of the melt-spun $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ samples to the nozzle's diameter during the melt-spinning process.

Key words: Bismuth antimony telluride, melt-spinning, spark plasma sintering, thermoelectric properties, nozzle.

Introduction

Melt-spinning (MS) is a rapid solidification technique that, compared with conventional solidification methods, produces microstructures with grain sizes at the sub-micron length scale, increased solubility of alloying elements and impurities, reduced levels of segregation, and in some cases the formation of metastable crystalline and amorphous phases [1-4]. These effects may lead to beneficial improvements in mechanical, magnetic, electrical, and

thermal properties in many alloy systems. Rapid solidification processing is therefore being used increasingly to manufacture metallurgical materials which take advantage of these improved properties in a variety of applications [1-4]. Quite recently, MS was applied to the synthesis of thermoelectric materials ($\text{Sb}_{2-x}\text{Bi}_x\text{Te}_3$ -family, skutterudites, ...) with improved thermoelectric performance due to positive influence of the obtained nano-microstructure on the Seebeck coefficient and thermal conductivity of such samples [5-11].

The melt-spinning technique involves quite complicated processes with a variety of experimental parameters that can be tuned for each new composition and according to the targeted property to be altered. The speed of the wheel, the heating temperature, the nozzle's diameter, the distance between the tube and the wheel's surface, the pressure in the chamber and the overpressure rate are all experimental parameters that influence the MS process. Some of these parameters are defined empirically and should be fixed in a quite narrow range to have successful melt-spinning processes resulting in numerous melt-spun ribbons or flakes with complex structure that may include some nano-sized grains as well as agglomerations of amorphous phases. In this work, we tested for the first time the influence of the nozzle's diameter on the thermoelectric properties of melt-spun $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ samples.

The densification of the melt-spun ribbons obtained was performed by Spark Plasma Sintering (SPS). This method is known as a successful technique for the preparation of nano-structured materials due to the short sintering time as a result of simultaneous actions of uniaxial pressure and pulsed electrical current. Thermoelectric properties including electrical resistivity, thermopower and thermal conductivity were measured between 5 and 460 K. These measurements were complemented by Hall effect experiments at low temperatures (5 – 300 K).

Experimental procedures

Stoichiometric amounts of high-purity elements in the form of granules (Bi, Sb and Te, 5N +, 99.999%) required to obtain the $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ composition were placed in quartz tubes (cleaned in acids and degased) and sealed, after having been maintained under secondary vacuum for 3 hours. The sealed tube was kept at 710°C during 5 hours in a vertical oscillating furnace and eventually quenched in a room-temperature water bath. The main part of the obtained ingot was used as a starting material for the MS processes. The other part was grinded with an agate mortar and densified by SPS during 5 minutes at 500°C under a pressure of 30 MPa, resulting in the sample called hereafter “reference sample”, which was not exposed to the MS procedure.

The ternary compositions based on the Sb_2Te_3 and Bi_2Te_3 are known to harbor deviations from the ideal stoichiometry and their strong sensitivity to the concentration of defects. Addition of Te was used in the starting composition in order to influence positively the charge carrier concentration and thus, the electrical properties of the samples. The Te atoms could create some interstitial defects in the material thereby adding electrons to the material and shifting the hole concentration to a level where the highest thermoelectric properties may be expected.

Figure 1 shows the external and internal design of the melt-spinner (Edmond Bühler) used in this work, which is equipped with a copper wheel of 198 mm in diameter that is cleaned with a polishing paste prior to each experiment. The end of the quartz tubes, wherein materials are loaded, is V-shaped (Fig. 2a) and nozzles of 0.5, 0.7 or 1.0 in diameter were drilled by ultrasonic drilling. This gives the possibility to use up to 10 g of raw material per process. The temperature inside the tube is constantly checked by a MAURER digital infrared pyrometer. The melt cooled on the wheel forms melt-spun “ribbons” or “flakes” of typical dimensions 3-5 mm in length, 0.5-3 mm in width, and 5-15 μm in thickness (Fig. 2b). Herein, the MS process was performed three times keeping all the parameters constant except for the nozzle’s diameter (replacing tubes with 1.0 mm, 0.7 mm and 0.5 mm in diameter of the nozzle). The three loads of melt-spun ribbons were obtained by ejection of the $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ ingot heated up to 620°C onto the copper wheel of \varnothing 19.8 cm rotating at 30 m/s linear speed using an overpressure of 0.2 bar. All samples were grinded in an agate mortar and densified in the same way as the reference sample with the same heating ramp and pressure applied.

Relative densities higher than 96% of the theoretical density were obtained for all samples. Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha 1$ radiation. The microstructural features of the melt-spun and reference samples were checked by scanning electron microscopy (SEM) using a XL30 FEG (Philips/FEI). For the transport properties measurements, samples with well-defined geometries and dimensions were prepared from dense ingots by cutting with a diamond-wire saw. Low-temperature measurements of Seebeck coefficient (S), thermal conductivity (κ), electrical resistivity (ρ) as well as Hall carrier concentration (p) were performed between 5 and 310 K using a physical property measurement system (PPMS, Quantum Design). From electrical resistivity and Hall measurements, the Hall mobility (μ_{H}) was calculated. ZEM-3 system (Ulvac-Rico) was used for the simultaneous measurements of S and ρ in the temperature range 320 – 460 K. Thermal diffusivity (a) was measured by a laser flash technique using a LFA 427 (Netzsch) in the same range of temperatures. This measurement was used to determine the thermal conductivity via the formula $\kappa = a \cdot c_p \cdot d$,

where c_p is the specific heat, measured with a DSC 404 F3 commercial system (Netzch), and d is the density of the SPS samples considered to be temperature-independent. Because the highest ZT values are obtained in the perpendicular direction, all physical properties were measured perpendicularly to the direction of uniaxial pressing of SPS.

Results and discussions

Figure 3 shows the PXRD patterns collected for the reference and melt-spun samples. All diffraction peaks correspond to the rhombohedral $Sb_{2-x}Bi_xTe_3$ -structure. The comparison of the patterns reveals the absence of evident structural differences between melt-spun samples regardless of the nozzle's diameter. In addition, the reference sample demonstrates significantly higher intensities of some reflections which correspond to the (0.0.15), (1.0.16) and (0.1.20) planes. This renormalization of the peak intensities can be explained by the slightly different grain orientation in this sample.

We performed some SEM investigations to see the specific structure of the melt-spun ribbons. The cross section view of a single ribbon (Fig. 4) demonstrates an average thickness of about 12 μm . The ribbons prepared with different nozzle's diameter possessed similar structure that corresponds to the data of PXRD investigations. Despite the fact that the samples were found to display minor structural differences, a direct link with the nozzle's diameter variation remains difficult to establish. A columnar structure can be clearly seen in the single ribbon along the direction perpendicular to the surface (Fig. 5a). The dendritic appearance of the free surface seems to result from the erratic growth in the basal planes. Close to the surface that was in contact with the copper wheel, a mixture of small sized particles up to one micrometer in size was regularly observed (Fig. 5b). This layer is less than 100 nm in thickness but introduction of such nano-sized grains was claimed to influence the behavior of all transport properties of melt-spun samples [10, 11].

The comparison between the transport properties of the reference sample and samples prepared via the MS process is shown in Figure 6. It can be noticed that all the melt-spun samples demonstrate minor differences in their transport properties, with no clear trend in the properties with the nozzle diameter. These results are in a good agreement with our previous conclusions based on PXRD and SEM investigations. Compared to the reference

material, a decrease in the total thermal conductivity with a concomitant increase in the electrical resistivity is observed. The values of the electrical resistivity are constant below $T < 20$ K for all the samples and increase above this temperature with increasing temperature. Taking into account the magnitude of ρ (from 2 to 15 $\mu\Omega\cdot\text{m}$), this behavior is typical of heavily-doped semiconductors.

The thermopower of the $\text{Sb}_{2-x}\text{Bi}_x\text{Te}_3$ samples is positive suggesting that electronic transport is dominated by holes as it is expected in these materials. The thermopower of all the samples increases with a maximum targeting near 440 K. Above this temperature, the thermopower decreases due to the influence of minority carriers. The values of the thermopower of the samples prepared using nozzle's diameter of 1.0 mm and 0.5 mm are similar and surpass both the results of the reference sample and those of the sample with nozzle' diameter 0.7 mm by about 7% above 300 K.

The temperature variation of the Hall carrier concentration (p -type) is the same whatever the sample is. Near room temperature, the values of the MS specimens are close to that of the reference sample except for the sample with a nozzle diameter of 0.7 mm which shows a higher carrier concentration. The variation in the carrier concentration is caused by a change in the amount of defects present in the samples. This is a well-known feature of the materials based on the Sb_2Te_3 or Bi_2Te_3 compounds. The Hall mobility is constant for all samples at low temperatures. Above 200 K, the Hall mobility follows nearly a $T^{-1.5}$ law, characteristic of charge carriers scattered by acoustic phonons. It is also seen that the Hall mobility values of the MS samples are degraded compared to the reference material.

All melt-spun samples show lowered thermal conductivity values compared to the reference sample by about 10%. This decrease may be explained by the introduction of additional grain boundaries that act as additional scattering points but also by an increasing of the electrical resistivity in the MS samples. The melt-spinning process results in a peak ZT value of 1.1 at 360 K for the sample prepared using a tube with a nozzle diameter of 1.0 mm. This value corresponds to an increase of 10% with respect to the reference material. The two other samples prepared through smaller nozzle diameters possess quite similar ZT values than the reference sample.

Conclusion

In this work, we report on a first study of the sensitivity of the melt-spun $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ samples to the variations in the diameter of the nozzle in the MS process. A set of three melt-spun samples was prepared using three different configurations of the tube, with nozzle' diameter of 1.0, 0.7 and 0.5 mm. The thermoelectric data were compared to those of a reference sample that did not undergo MS. All samples were densified by the SPS technique and showed high density (over 96% of the theoretical density). The PXRD and SEM investigations did not reveal any structural differences between the different melt-spun samples. Despite this, slight deviations in their transport properties were found to be present. A maximum ZT close to 1.1 at 360 K was achieved in the sample prepared using a nozzle diameter of 1.0 mm. The two other samples prepared with smaller nozzle diameters were found to show properties quite similar to the reference sample. This may be explained by variations in the ejection speed of the melt through the nozzle. In other words, the smaller the diameter of the nozzle was, the longer the time it took for the melt to go out from the tube. Thus, a local overheating possibly could take place thereby influencing the transport properties.

Acknowledgments

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Figure captions

Fig. 1. Edmund Bühler melt-spinner used in this work: (left-hand side) general view; (right-hand side) inner chamber design with main parts indicated by numbers and arrows, where 1 – tube with a nozzle, 2 – induction coil, 3 – copper wheel, 4 – material collector.

Fig. 2. a) The melt-spinning tube with V-shaped bottom and nozzle indicated by an arrow; b) collected melt-spun ribbons.

Fig. 3. PXRD patterns obtained from the grinded reference (black colour) and melt-spun samples of $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ prepared using nozzle's diameter of 1.0 mm (red colour), 0.7 mm (blue colour) and 0.5 mm (green colour). The main diffracting planes of the structure are mentioned in brackets.

Fig. 4. SEM image of the cross-section of a single melt-spun ribbon. The scale bar corresponds to 10 μm .

Fig. 5. High magnification of SEM images of a cross-section of a ribbon: a) close to the free surface, showing columnar structure that creates dendritic surface of one side of the ribbon; b) close to the contact surface, showing the layer of the small grain-size particles below 1 μm . The scale bars corresponds to 5 and 1 μm , respectively.

Fig. 6. Temperature dependence of (a) electrical resistivity, (b) thermopower, (c) hole concentration, (d) Hall mobility, (e) total thermal conductivity and (f) ZT of the reference (black open circle) and melt-spun $\text{Sb}_{1.6}\text{Bi}_{0.4}\text{Te}_{3.1}$ samples prepared via melt-spinning with variation in nozzle's diameter (red filled circle: 1.0 mm, blue filled square: 0.7 mm, green filled diamond: 0.5 mm). Measurements were performed along the direction perpendicular to the pressing direction.