L.D. Ivanova[1], V.V. Molokanov[1], A.V. Krutilin[1], P.P. Umnov[1], N.V. Umnova[1], O.N. Uryupin[2], A.A. Shabaldin[2]

[1]Federal State Budget Institution of Science A.A. Baikov Institute for Metallurgy and Materials Science of the RAS, 49, Leninsky prosp., Moscow, 119991, Russia;
[2]Federal State Budget Institution of Science A.F. Ioffe Physical-Technical Institute of the RAS, 26, Politechnicheskaya Str., Saint-Petersburg, Russia

USE OF THE TAYLOR-ULITOVSKY METHOD TO PREPARE THERMOELECTRIC MATERIALS OF BISMUTH AND ANTIMONY TELLURIDE SOLID SOLUTION

Conditions for producing glass-coated wires of bismuth and antimony telluride solid solution using the Taylor-Ulitovsky method have been investigated. The influence of coating materials (the type of glass) and drawing rate on the process of formation of wires of different diameter has been studied. The optimal conditions for producing extended wires (up to 1 m) with the core diameter from 100 to 250 μm and stable in length geometrical parameters have been established. The structure of wire breaks has been investigated though use of scanning electron microscopy. The Seebeck coefficient has been measured in the range of temperatures 70 to 420 K as a function of wire diameter. The outlook for using the Taylor-Ulitovsky method to produce rather thin legs of microcoolers that cannot be cut of currently employed materials has been shown.

Key words: Taylor-Ulitovsky method, microwires, solid solution of bismuth and antimony tellurides, Seebeck coefficient.

Introduction

Thermoelectric power converters have gained wide application nowadays in a variety of science and technology fields. Particularly topical is the problem of thermoelectric device efficiency improvement. At the present time, attention has been focused on studying the possibility of considerable increase of thermoelectric figure of merit of materials due to their nanostructuring. Thermoelectric materials based on nanopowders are in research and development stage in our country, as well as abroad. Theory predicts increase in ZT of nano-sized thermoelectric material to 3.5 only in the case when grain size will be less than 10 nm [1]. Until the present time, the bulk thermoelectric materials with grain size on the level of nanometer units have not been obtained yet. There are experimental works presenting the data on materials with highly dispersed structure for which ZT reaches the values of 1.2 to 1.5 [2, 3]. Fabrication of glass-coated microwires by Taylor-Ulitovsky method based on Bi и Bi_2Te_3 is reported in the literature [4-7]. The possibility of considerable increase of thermoelectric figure of merit of material in this structure is indicated. In a number of cases, microcoolers with the leg size less than hundreds of microns are required. Therefore, in the development of new types of microcoolers, of interest can be microwires based on solid solutions of p- and n-type bismuth and antimony chalcogenides with sufficiently high thermoelectric figure of merit.

The purpose of this work is to develop conditions for preparation of $Bi_{0.5}Sb_{1.5}Te_3$ solid solution in the form of glass-coated wires using the Taylor-Ulitovsky method.

Preparation of $Bi_{0.5}Sb_{1.5}Te_3$ solid solution by the Taylor-Ulitovsky method

According to this method, material placed in a glass tube is melted and, together with a coating which is softened, is drawn at a certain rate. The schematic of microwires fabrication is shown in Fig. 1.

As an original material use was made of a single crystal of Czochralski grown solid solution $Bi_{0.5}Sb_{1.5}Te_3$ [8]. The melting point of this material was 610 °C. The single crystal had a well-expressed layered crystalline structure typical of materials with tetradymite structure. A chip of this single crystal is represented in Fig. 2. Cleavage planes are clearly seen that are arranged perpendicular to the main crystallographic axis *c*.

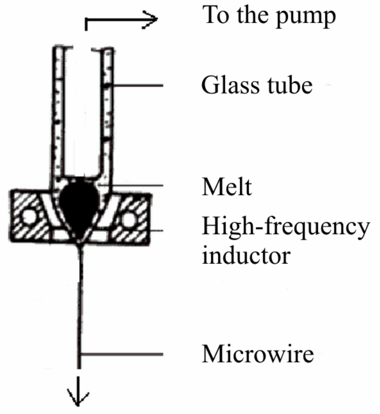

Fig. 1. Schematic of glass-coated thin wires fabrication from the melt by the Taylor-Ulitovsky method.

The experiments in this work were performed with the use of glass tubes made of various types of glass: silicate, molybdenum, borate (pyrex) with different softening temperatures from 500 to 750 °C. Typical appearance of the resulting wires of thermoelectric material with a coating of these glasses is shown in Fig. 3 *a*, *c*. It was established that with the use of tubes of low-melt silicate glass with softening temperature 500 − 580 °C possessing low thermal stability, cracking of glass coating takes place on the wire samples (Fig. 3 *a*). Molybdenum and pyrex glasses are more temperature-resistant (Fig. 3 *b*). However, to fabricate wires in tubes of these glasses, the melt must be overheated to temperatures 950 – 1100 °C. In this work, melt temperature ~ 950 °C was maintained. As was established later, such overheat resulted in tellurium evaporation and a change in wire material composition, as compared to the original material, since the process was not carried out from closed volume.

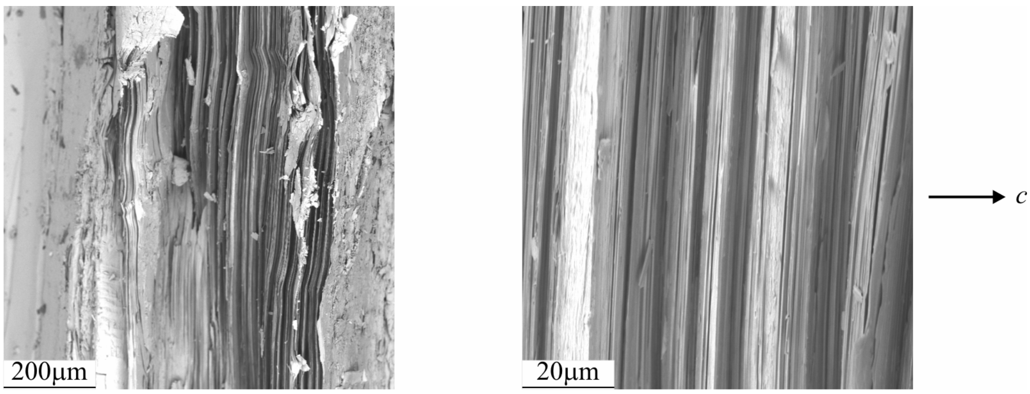

Fig. 2. SEM image of a chip of the original single crystal $Bi_{0.5}Sb_{1.5}Te_3$ obtained with different magnification.

The effect of drawing rate on the process of formation of wires of different diameter was investigated. The wires of material in pyrex and molybdenum glass coating with core diameter from 2 mm to 0.1 mm of 1 m in length were obtained. Investigations performed on scanning electron microscope have shown that the surface of material adjacent to the glass is smooth, glossy, without visible defects (Fig. 2 *b*). It has been established that samples of wires with the core diameter from 100 to 250 μm retain their cylinder shape (Fig. 3 *a*, *c*) with drawing rates from 1 m/s to 0.05 m/s. Core breaks have a directed crystalline layered structure with well-expressed cleavage planes typical of these materials (Fig. 3 *d*, *e*). Further reduction of drawing rate (less than 0.05 m/sec) results in the distortion of core section, namely the diameter assumes the shape of an ellipse (Fig. 3 *f*).

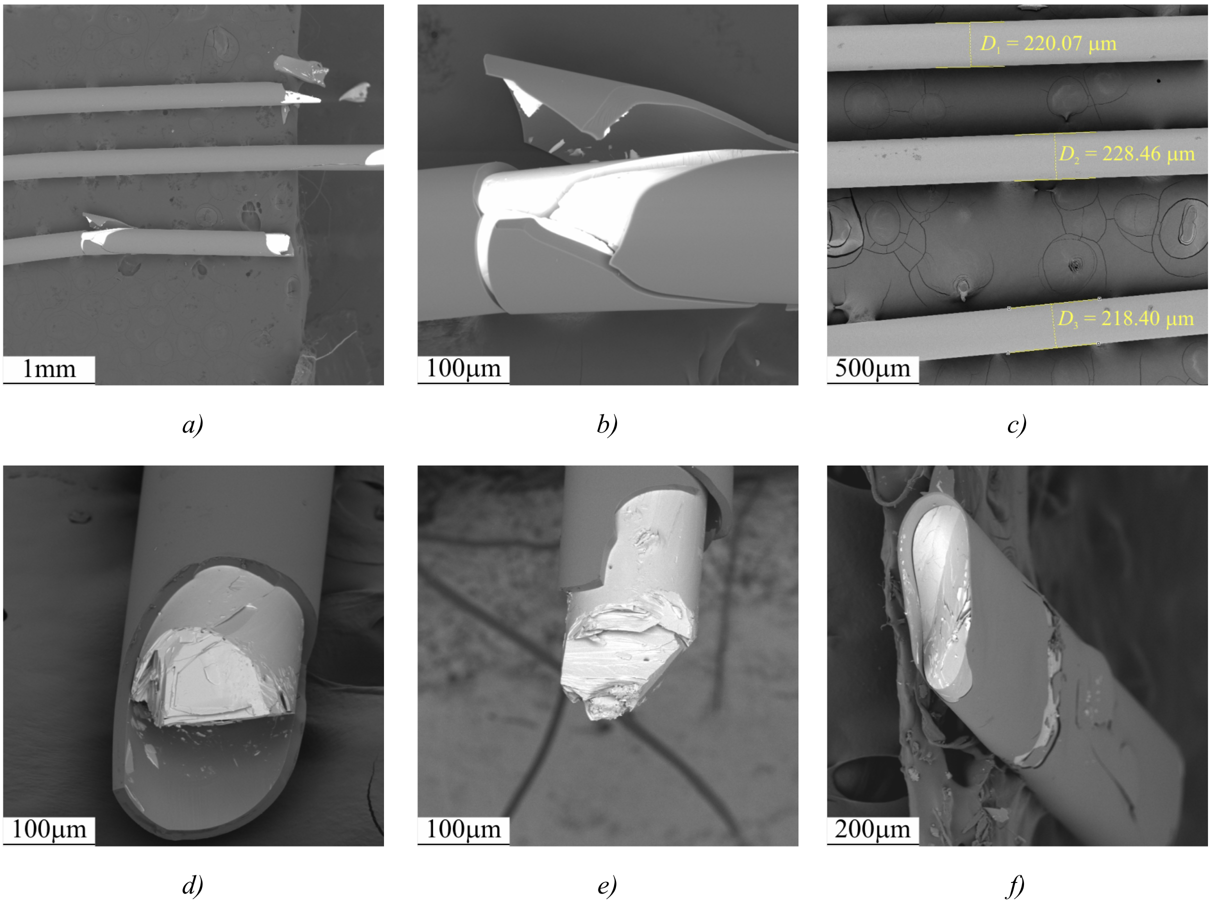

Fig. 3. Wires (a, c) and breaks (b, d, e, f, g) in glass-coated $Bi_{0.5}Sb_{1.5}Te_3$: molybdenum glass (a, b), pyrex (c, d, e, f, g). Drawing rates 0.1 m/s (a, b, c, d, e), 0.03 m/s (f).

The Seebeck coefficient of the wires

The Seebeck coefficient is known to be one of the most informative characteristics of thermoelectric materials. This parameter does not depend on sample geometry and, by its value, one can judge of current carrier concentration in the measured material. In Saint-Petersburg, an experimental setup was developed for measuring the Seebeck coefficient of quantum-size nanowires in the range of temperatures 80 to 400 K by the relative method [9]. Measurements are performed in a vacuum chamber. Calibrated constantan is used as a reference. Temperature difference is created by heat flux from the source of light incident on thermal radiation detector. The temperature dependence of the Seebeck coefficient of object under study is measured simultaneously with the Seebeck coefficient of the reference. The accuracy of measurement over the entire range of temperatures is estimated as 12 %.

Fig. 4 represents the temperature dependences of the Seebeck coefficient for wires of different diameter (represented together with glass coating) and a single crystal used as the original ingot. The results obtained are compared to the Seebeck coefficient of this single crystal measured by the absolute method in given temperature range (Fig. 4, curve 4).

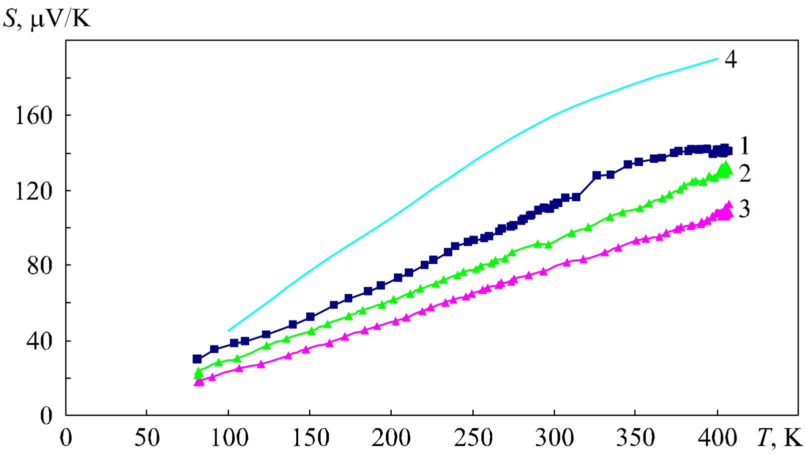

Fig. 4. Temperature dependences of the Seebeck coefficient for glass-coated $Bi_{0.5}Sb_{1.5}Te_3$ wires; outside diameter 0.2 mm (1), 0.3 mm (2), 0.4 mm (3) and the original ingot (4).

It was established that the wires have lower Seebeck coefficient values than the original single crystal over the entire range of temperatures. In so doing, a thinner wire (outside diameter 200 μm, curve 1) is matched by higher Seebeck coefficient values. The above effect can be due to strong stresses created by glass coating [6, 10]. On the other hand, it is known that the Seebeck coefficient value depends on the degree of material composition deviation from stoichiometric composition towards tellurium deficit. Thus, the composition of solid solution generally used in the products can be represented as $Bi_{0.5}Sb_{1.5}Te_{3-x}$ ($0.005 \leq x \leq 0.08$), and in the region of tellurium solubility (~ 0.2 at. %) charge carrier concentration can vary several times and, accordingly, the Seebeck coefficient at room temperature can change from 80 to 220 μV/K [11]. Therefore, with increase in the degree of deviation of solid solution composition toward tellurium decrease, there is increase in carrier concentration and, accordingly, decrease in the Seebeck coefficient. Experiments on formation of the wires were conducted with open melt surface, from which volatile components were evaporated. For glass softening the melt was overheated to temperature ~ 950 °C, whereas ingot melting temperature was ~ 610 °C. Exactly for this reason, thermoelectric materials in the form of glass-coated wires had a higher current carrier concentration and, accordingly, a lower Seebeck coefficient than the original single crystal.

To produce materials with a lower carrier concentration, corrections must be introduced into process technology, to assure correspondence to given composition and take into account the effect of stresses created by glass coating.

Conclusions

The task of producing the legs for microcoolers has been solved with the aid of the Taylor-Ulitovsky method, using the variant of forced melt drawing similar to known method of fiber glass fabrication. The effect of coating materials and drawing rates on core formation processes in $Bi_{0.5}Sb_{1.5}Te_3$ solid solution has been investigated. Optimal conditions for producing sufficiently extended wires (to 1 m) of stable form with the core diameter from 100 to 250 μm have been established. Wires with the Seebeck coefficient from 100 to 140 μV/K at 400 K have been produced.

For conformity between core composition and the original ingot composition it is required to ensure formation of wires with closed melt volume.

The work has been performed with the financial support of Russian Foundation for Basic Research Project № 13-08-00041 a.

References

1. L.D. Hicks, T.C. Harman, and M.S. Dresselhaus, Use of Quantum-Well Superlattices to Obtain a High Figure of Merit from Nonconventional Thermoelectric Materials, *Appl. Phys. Lett*. **63** (23), 3230 − 3232 (1993).
2. B. Poudel, Q. Hao, Yi Ma, Y.C. Lan, A. Minnich, Bo Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X.Y. Chen, Y.M. Lui, M.S. Dresselhaus, G.G. Chen, and Z. Ren, High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys, *Science* **320** (5876), 634 – 638 (2008).
3. W. Xie, X. Tang, Y. Yan, and T. Tritt, Unique Nanostructures and Enhanced Thermoelectric Performance of Melt-spun *BiSbTe* Alloys, *J. Appl. Phys*. **94**, 102111/1-3 (2009).
4. A.A. Nikolaeva, L.A. Konopko, A.K. Tsurkan, and O.V. Botnar, Anisotropy of Thermoelectric Properties of *Bi* and *Bi-Sn* Nanowires for Thermoelectric Applications, *Metallofizika i Noveishie Technologii* **33** (1), 77 – 85 (2011).
5. D. Meglei, M. Dantu, S. Donu, and A. Russu, Microthermocouple of Bifilar Microwires Based on Bi_2Te_3 Thermoelectric Materials, *J. Thermoelectricity* **2**, 61 – 65 (2009).
6. I.A. Popov, P.P. Budyul, E.F. Moloshnik, and O.V. Botnar, Increase of Thermoelectric Figure of Merit of $Bi_{1-x}Sb_x$ Thin Wires under Elastic Tension in a Magnetic Field, *J. Thermoelectricity* **2**, 37 – 46 (2008).
7. I. Shiota, H. Kohri, M. Kato, and I.J. Ohsugi, Fine Bi_2Te_3 Wires Fabricated by Glass Sealed Melt Spinning, *Proc. 25th International Conference on Thermoelectrics* (2006), pp. 247 – 251.
8. L.D. Ivanova, Yu.V. Granatkina, Single Crystals of Solid Solutions of *p*-type Bismuth and Antimony Chalcogenides Intended for Cooling to $T < 150$ K, *Inorganic Materials* **37**(2), 199 − 202 (2001).
9. O.N. Uryupin, A.A. Shabaldin, Procedure for Measurement of the Seebeck Coefficient in Quantum Semiconductor Wires, *Thermoelectrics and their Application* (Saint-Petersburg, 2006), pp. 346 − 350.
10. P.P. Umnov, N.V. Kurakova, Yu.S. Shalimov, M.I. Pertzhik et al., Effect of Stresses Created by Glass Encapsulation on Melt Solidification Process when Manufacturing a Microwire of Magnetically Soft Alloy $Co_{69}Fe_4Cr_4Si_{12}B_{11}$, *J. Advanced Materials* **1**, 79 – 85 (2009).
11. N. Kh.Abrikosov, V.F. Bankina, L.A. Kolomoyets, and N.V. Dzhamashvili, Deviation of Solid Solution from Bi_2Te_3-Sb_2Te_3 Stoichiometric Cut in the Field of $Bi_{0.5}Si_{1.5}Te_3$ Composition, *Izvestia AN SSSR: Inorganic Materials* 13 (5), 827 − 829(1977).

Submitted 22.07.2013.