Study of the Hot Extruded Alloys of the Bismuth and Antimony Chalcogenides Solid Solutions

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Abstract

The authors have investigate thermoelectric properties and a microstructure of the materials based on solid solutions of n-type and p-type Bi_2Te_3–Sb_2Te_3 and Bi_2Te_3–Bi_2Se_3 systems, and produced by method of hot extrusion. Doped alloys with different concentrations of charge carriers have been produced (Seebeck coefficient at the room temperature varied from $|160|$ to $|315|$ µV/K). Seebeck coefficient, electrical and thermal conductivity of ingots were measured for a 100-400 K temperature range. It has been found that the theory explaining the mechanisms of diffusion in materials produced based on the above mentioned solid solutions and intended for alloys produced by methods of directed crystallization is also applicable for alloys produced by method of extrusion. The compositions have been designed for extruded materials with high thermoelectric figure of merit at different temperatures, which is not inferior to that of single crystals grown by the Czochralski method.

Introduction

Materials produced on the basis of antimony and bismuth chalcogenide solid solutions are used in thermoelectric coolers and generators intended for different applications. Today, there is a pressing need for the enhancement of thermoelectric cooling due to the application of new efficient materials for various cascades of thermoelectric coolers. It can be realizable due to the application of TE legs having the properties optimized for different temperature ranges. For the production of such materials use is made of the extrusion method, i.e. hot extruding through an extrusion die. This method is a high-performance forming process and also a technique providing for significant enhancement of the mechanical strength of thermoelectric materials without reducing their high thermoelectric figure of merit. The paper describes the best conditions of extrusion and the optimal compositions of extruded with high thermoelectric figure of merit at different temperatures in a 100-400 K region.

Experimental

The method of hot extrusion of the materials on the basis of solid solutions of p-type and n-type Bi_2Te_3–Sb_2Te_3 and Bi_2Te_3–Bi_2Se_3 systems consists of several stages. The material synthesized in quartz ampoules evacuated to 0.1 Pa was crushed down, briquetted and annealed. The annealed briquettes were fed into a heated container and extruded through a die. The rods were annealed in the inert gas atmosphere. The temperature of synthesis, extrusion and annealing was calculated based on thermodynamic design of the compositions of the condensed and gas-vapour phases within a temperature range of 200-1200 K. Such calculations were made for every investigated composition. For this research 10 mm diameter rods of 120 mm length were produced.

The microstructure of rods was investigated throughout the cross-sectional area and lateral area after thin section pickling treatment during 20 s in a 50% HNO_3 aqueous solution.

Thermoelectric characteristics of rods: Seebeck coefficient α, electrical conductivity σ, thermal conductivity κ, were measured in a 100-400 K temperature range. Thermoelectric figure of merit Z was calculated from the formula $Z=\alpha^2\sigma/\kappa$. Lattice component of thermoelectric figure of merit was calculated from the formula: $\kappa_l = \kappa - \kappa_e$, where $\kappa_e=L\sigma T$ (L – Lorenz number).

Materials of p-type conductivity

The research was undertaken into materials produced based on Bi_2Te_3–Sb_2Te_3 system solid solutions with 15 to 30 mole% Bi_2Te_3 content.

It is known that a bismuth and antimony telluride solid solution in case of crystallization departs from the stoichiometric composition towards the excess of bismuth and antimony atoms and the solubility region of tellurium is less than 0.2 at.%. Within the solubility region of tellurium the concentration of charge carriers changes significantly. Minor variations of tellurium content in the region of the composition of $Bi_{0.5}Sb_{1.5}Te_3$ solid solution result in the variation of the Seebeck coefficient at the room temperature of these alloys from 130 to 250 µV/K [1]. Thus, a material with low concentration of charge carriers (high α value) can be produced with the maximum possible solubility of tellurium in the solid solution. Selenium doping also allows lower concentration of charge carriers in these materials.

Extruded alloys were produced with different concentrations of charge carriers (at the room temperature α varied from 160 to 315 µV/K).

Research into the microstructure has shown that in case of extrusion alloys are affected by plastic deformation resulting in the formation of a re-crystallized fine-grained polyhedral structure without any traces of

deformations both in section and along the direction of extrusion of a sample. (Fig. 1). Grain size ranged from 2 to 30 μm.

a   *b*   *c*
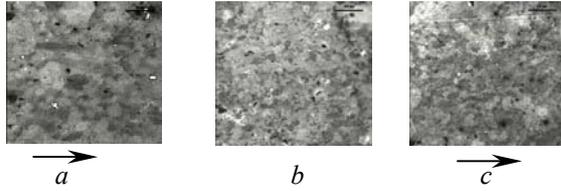
Fig. 1. The microstructure of $Bi_2Te_3 - Sb_2Te_3$ solid solution extruded alloys with different values of Seebeck coefficient at the room temperature: 295 (a), 315 (b), 170 μV/K (c), in parallel (a, c) and perpendicularly (b) to extrusion direction, (x1000). Arrows show the direction of extrusion.

Table 1. Room-temperature thermoelectric parameters: Seebeck coefficient (α_r), electrical conductivity (σ), total and lattice thermal conductivities (κ and κ_l), thermoelectric figure of merit (Z) of Bi_2Te_3–Sb_2Te_3 solid solution extruded (no.1 through 4) and for the single crystal grown by Czochralski method (no.5).

sample no.	Composition	α_r, μV/K	σ, S/cm	$\kappa \times 10^3$, W/cmK	$\kappa_l \times 10^3$, W/cmK	$Z \times 10^3$, 1/K
1	$Bi_{0.3}Sb_{1.7}Te_3$	166	1600	15.1	6.8	2.92
2	$Bi_{0.6}Sb_{1.4}Te_3$	208	961	12.8	8.2	3.25
3	$Bi_{0.6}Sb_{1.4}Te_3$	296	168	9.1	8.3	1,62
4	$Bi_{0.57}Sb_{1.43}Se_{0.15}Te_{2.85}$	312	210	7.7	6.75	2,65
5	$Bi_{0.6}Sb_{1.4}Te_3$, Se-doped	226	783	13.0	9.3	3.06

In samples characterized by high values of Seebeck coefficient (at 300 K α = 295 и 315 μV/K) (Fig. 1*a* and 1*b*) some fine white-colour eutectic tellurium-based precipitates were found differing in shape from grains of solid solution. The presence of eutectic shows that the composition of these samples is on the boundary of the tellurium solubility region. In this case the amount of tellurium-based eutectic was larger in a sample with α_r = 295 μV/K. A sample with high value of α_r = 315 μV/K was characterized by finest grain size and clearer grain boundaries. In a sample with low value of α_r = 170 μV/K tellurium eutectic precipitates were actually not observed. (Fig. 1*c*).

The results of measurement of thermoelectric properties of extruded materials (no.1 through 4) at the room temperature and within a 100-400 K temperature range and the data [2] on a single crystal grown by Czochralski method (no.5) are given in the Table 1 and in Fig. 2. The greatest thermoelectric figure of merit at the room temperature was observed in the materials with α_r = (210–220) μV/K, in this case Z = (3.1–3.2) $\times$ 10^{-3} K^{-1} both for extruded and for the single crystal grown by Czochralski method.

The shift of the maximum Z value to the region of higher temperatures was observed for the materials with low concentration of charge carriers (high α_r value), in this case the Se-doped composition (no.4) was characterized by the highest Z in the region of 150-200 K.
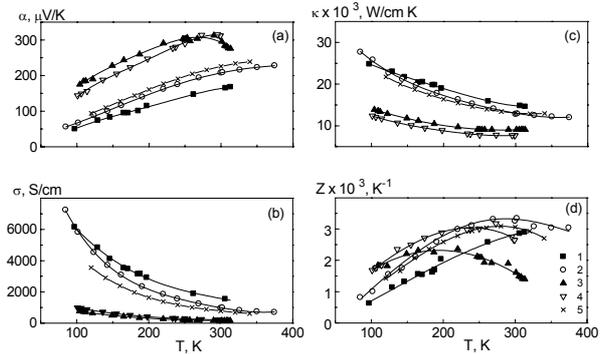
Fig. 2. Temperature dependences of Seebeck coefficient α (a), electrical conductivity σ (b), thermal conductivity κ (c) and thermoelectric figure of merit Z (d) of the extruded (1 through 4) and single crystal (5) materials. The numbers of curves correspond to the numbers of samples presented in the Table 1.

The $\alpha(\ln T)$, $\lg\sigma$ ($\lg T$), $\lg\kappa_l(\lg T)$ dependences were plotted and the slopes of curves were calculated relative to the respective coordinate axes (Fig. 3). For samples Nos 1 through 5 the slope α ($\ln T$) was 140±5 μV/K, for σ ~ T^{-m} dependence m = (1,47–1,75) and κ_l ~ T^{-s} s = (0,37−0,48). The slopes of these curves for the extruded alloy (no.2) and for a single crystal (no.5) characterized by a similar α_r value were alike. For these samples in the region of 100-300 K temperatures the slope of $\alpha(\ln T)$ dependences corresponds to 145 μV/K, σ~$T^{-1.7}$, κ_l~$T^{-0.37}$.

Table 2. Room temperature thermoelectric parameters: Seebeck coefficient (α_r), electrical conductivity (σ), total and lattice thermal conductivities (κ and κ_l), thermoelectric figure of merit (Z) of Bi_2Te_3–Sb_2Te_3 solid solution extruded (no.3 through 6) and single crystals grown by Czochralski method (no.1 and 2).

sample no.	Composition	α_r, μV/K	σ, S/cm	$\kappa \times 10^3$, W/cmK	$\kappa_l \times 10^3$, W/cmK	$Z \times 10^3$, 1/K
1	$Bi_2Te_{2.85}Se_{0.15}$	-206	1200	16.4	10.7	3,1
2	$Bi_2Te_{2.85}Se_{0.15}$	-273	440	13.3	11.4	2.5
3	$Bi_2Te_{2.82}Se_{0.18}$	-215	1030	15.4	10.1	3.0
4	$Bi_2Te_{2.82}Se_{0.18}$	-295	225	11.1	9.9	2.0
5	$Bi_2Te_{2.1}Se_{0.9}$	-245	325	10.3	8.8	1.9
6	$Bi_2Te_{1.8}Se_{1.2}$	-240	323	10.7	9.2	1.7
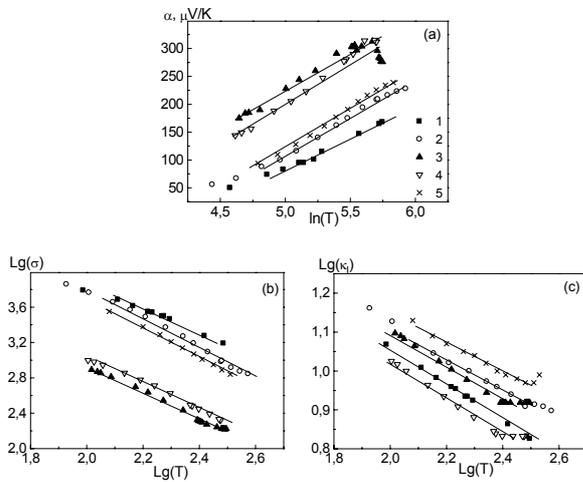
Fig. 3. Logarithmic relationships of Seebeck coefficient α (a), electrical conductivity σ (b) and lattice thermal conductivity κ_l (c) of extruded materials (1 through 4) and of the single crystal (5) with different concentrations of charge carriers. The numbers of the curves correspond to the numbers of samples presented in the Table 1.

To identify the cascades of TE coolers operating in a 100-300 K temperature region, for which the investigated materials are most suitable, the mean values Z_{mean} were calculated of thermoelectric figure of merit. For coolers operating at a 200-300 K temperature of the hot end high $Z_{mean} = 3,1 \times 10^{-3}$ K^{-1} is characteristic of extruded with $\alpha_r = 210$ μV/K. The highest thermoelectric figure of merit at temperatures below 200 K ($Z_{mean} = 2,7 \times 10^{-3}$ K^{-1} within a 200-150 K temperature range and $Z_{mean} = 2,0 \times 10^{-3}$ K^{-1} within a 150−100 K temperature range) is characteristic of containing selenium extruded alloy with $\alpha_r = 312$ μV/K, with the composition on the boundary of the maximum solubility of tellurium in the region of this solid solution.

Materials of n-type conductivity

Bi_2Te_3–Bi_2Se_3 solid solution n-type thermoelectric materials were extruded with a 6 to 40 mole % content of Bi_2Se_3 and different concentrations of charge carriers (at

the room temperature the Seebeck coefficient varied from -206 to -295 μV/K).

The research into the microstructure showed that the structure of the samples depended on their composition. Bi_2Te solid solution alloy containing up to 14 mole% of Bi_2Se_3 had the polyhedral structure of grains, that is typical of recrystallized alloys (Fig. 4a). With the increase of Bi_2Se_3 concentration the flow lines appeared inside the grains of solid solution that is an evidence of solid solution decomposition with the formation of the Bi_2Te_2Se ternary compound (Fig. 4b).

a   *b*
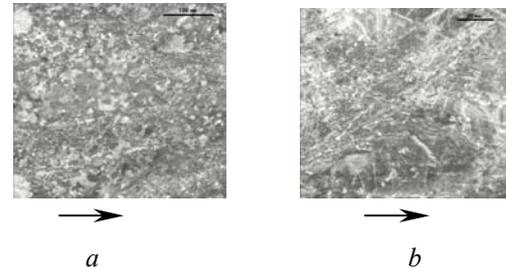
Fig. 4. The microstructure of extruded $Bi_2Te_{2.82}Se_{0.18}$ (a), x400 and $Bi_2Te_{1.8}Se_{1.2}$ (b), x1000 along the direction of extrusion. Arrows show the direction of extrusion.

The results of measurement of thermoelectric properties of extruded (no.3 through 6) at the room temperature are shown in the Table 2. For the sake of comparison the data is also presented on the properties of single crystals no.1 and 2 grown by Czochralski method [3]. The highest thermoelectric figure of merit was observed in extruded material with $\alpha_r = −215$ μV/K, for which Z value was 3×10^{-3} K^{-1}. For the best single crystals materials with a similar value of α_r it is possible to achieve $Z \cong 3 \times 10^{-3}$ K^{-1}.

Fig. 5 shows temperature dependences of α, σ, κ and Z within a 100-400 K temperature range for extruded and single crystal materials, their compositions are given in the Table 2.

High Z values within 300−250 and 250−100 K temperature ranges are characteristic of halogenide-

doped extruded of $Bi_2Te_{2.82}Se_{0.18}$ composition, with $\alpha_r = -215$ μV/K and $\alpha_r = -295$ μV/K accordingly.
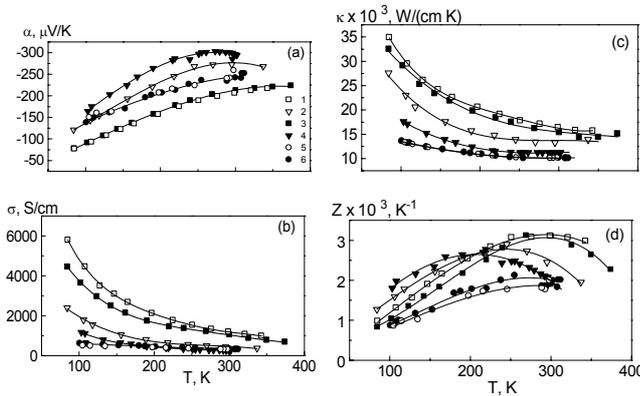
Fig. 5. Temperature dependences of the Seebeck coefficient α (a), electrical conductivity σ (b), thermal conductivity κ (c) and thermoelectric figure of merit Z (d) of single crystals (1,2) and extruded materials (3 through 6). The numbers of curves correspond to the numbers of samples presented in the Table 2.

The $\alpha(\ln T)$, $\lg\sigma(\lg T)$, $\lg\kappa_l(\lg T)$ dependences were plotted and the slopes of curves were calculated relative to the respective coordinate axes in the 100-250 K temperature region for extruded and single crystal samples (Fig. 6).
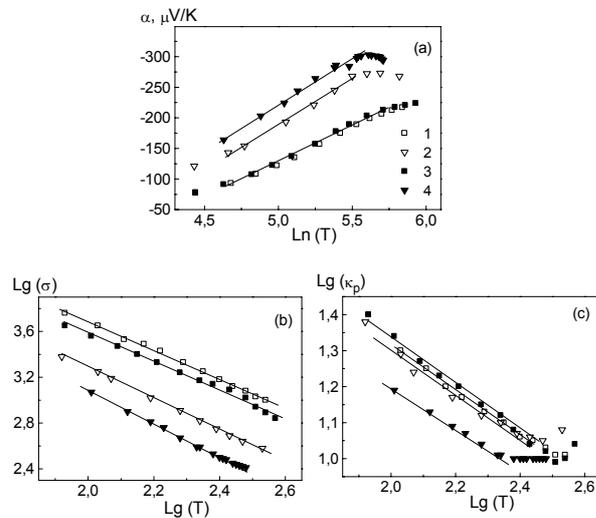
Fig. 6. Logarithmic relationships of Seebeck coefficient α (a), electrical conductivity σ (b) and lattice thermal conductivity κ_l (c) of the single crystals (1,2) and extruded materials (3,4) with different concentrations of charge carriers. The numbers of the curves correspond to the numbers of samples presented in the Table 2.

Temperature dependences of these parameters for $Bi_2Te_{2.85}Se_{0.15}$ solid solution single crystals (no. 1 and no. 2, see the Table 2), with different concentrations of charge carriers grown by Czochralski method were produced in [3].

It can be seen that for samples with similar concentrations of charge carriers, perspective of production method, the slopes of these dependences are alike, i.e., the theory explaining the mechanisms of diffusion in materials produced by method of directed crystallization [2,3,4] is applicable to the materials produced by method of extrusion.

For materials with $\alpha_r = -206$ and -215 μV/K (curves 1 and 3) the slope α (lnT) corresponds to 107 μV/K, $\sigma \sim T^{-1.25}$, $\kappa_l \sim T^{-0.6}$. For materials with $\alpha_r = -273$ and -295 μV/K (curves 2 and 4) the curve slopes α(lnT), lgσ(lgT), lgκ_l(lgT) correspond to 148 μV/K, ~1.4 и ~0.6 accordingly.

Conclusions

Thermoelectric materials of p- and n-type $Bi_2Te_3-Sb_2Te_3$ and $Bi_2Te_3-Bi_2Se_3$ systems were produced by method of extrusion. These materials are characterized by thermoelectric figure of merit, which is not inferior to that of single crystals grown by Czochralski method. In this case, the highest thermoelectric figure of merit at a temperature below 200 K is characteristic of extruded materials with low concentration of charge carriers (Seebeck coefficient $\alpha_r \sim |300|$ μV/K). It was found that the theory explaining the mechanisms of diffusion in materials of the above mentioned systems, which had been developed for alloys produced by methods of directed crystallization, was true also for the materials produced by method of extrusion.

References

1. Abrikosov N.Ch. *et al.*, "Deviations from Stoichiometry in the $Bi_{0.5}Sb_{1.5}Te_3$ Solid Solution" *Izv. AN SSSR, Neorgan. Mater.* vol.13, no. 5 (1977), pp. 827-829 (in Russian).
2. Ivanova L.D., Granatkina Yu.V. "Thermoelectric Properties of Bi_2Te_3-Sb_2Te_3 Single Crystals in the Range 100-700 K" *Inorganic Materials* vol. 36, no. 7 (2000), pp.672-677.
3. Svechnikova T.E., Konstantinov P.P., Alekseeva G. T. "Physical Properties of $Bi_2Te_{2.85}Se_{0.15}$ Single Crystals Doped with Cu, Cd, In, Ge, S or Se" *Inorganic Materials* vol. 36, no. 6 (2000), pp.556-560.
4. *Gol'tsman, B.M., Kudinov, V.A., and Smirnov, I.A., Poluprovodnikovye termoelectricheskie materialy na osnove* Bi_2Te_3 (Bi_2Te_3-Based Thermoelectric Semiconductors), Moscow: Nauka, 1972.320c.