Development of technology for high-strength thermoelectrics with a diameter of up to 35 mm based on Bi_2Te_3 polycrystals by hot extrusion

© A.I. Sorokin, M.S. Ivantsov, N.Yu. Tabachkova, V.T. Bublik, S.Ya. Skipidarov, Z.M. Dashevsky

RusTek LLC,
109383 Moscow, Russia

E-mail: almaz_gx@mail.ru

Received August 18, 2021
Revised August 25, 2021
Accepted August 25, 2021

Hot extrusion of thermoelectric materials of large diameters is associated with the problem of preserving the deformation texture in them both in length and in cross-section. The paper shows for the first time the technology of obtaining polycrystals based on Bi_2Te_3 *n*- and *p*-type conductivity with a diameter of up to 35 mm, by hot extrusion. Detailed studies of the structural properties have been carried out. The mechanical properties (strength) of the crystals were measured. The thermoelectric properties of polycrystals of various diameters (the coefficient of thermal EMF α, electrical conductivity σ and figure of merit Z by the Harman method) were measured. It is shown at the optimal technology polycrystals based on Bi_2Te_3 *n*- and *p*-type conductivity with a diameter of 35 mm were produced, which are comparable in thermoelectric and mechanical properties with polycrystals of traditional diameter (25 and 30 mm), which are currently commercially produced.

Keywords: thermoelectricity, Bi_2Te_3, extrusion, thermoelectric properties, mechanical properties.

DOI: 10.21883/SC.2022.01.53114.07

1. Introduction

Any present-day production of thermoelectric products (coolers, thermostats, autonomous energy converters) starts with development of technology for production the thermoelectric materials. There are two main methods of production of perfect thermoelectric materials based on Bi_2Te_3: direct crystallization from melting and hot extrusion [1–8]. One of the important advantages of extruded thermoelectric materials based on Bi_2Te_3 is higher mechanical strength compared to materials, produced by crystallization from melting [6,9–13]. Mechanical properties are essential in using the materials in thermoelectric converters (modules), which branches are subject to high thermal voltages due to large temperature difference during their operation [11].

The purpose of this study is development of technology of producing the rods based on Bi_2Te_3 with diameter $d = 35$ mm by hot extrusion method. This approach allows to increase performance of thermoelectric materials producing, while decreasing the thermoelectric material wastes during cutting, that eventually affects the product cost.

2. Samples preparation and study methods

Synthesis of materials based on Bi_2Te_3 of *n*- and *p*-type of conductivity was performed by melting the components in inert atmosphere at the developed plant (SM, RusTec). The advantages of this method are simplicity, high performance and ease of combining the primary synthesis from initial components and wastes after cutting. The resulting synthesized material was subject to mechanical and activation processing at turbo-mill (TurboM-1, RusTec). 250-ton press (IP2500Auto, ZIPO) was used for extrusion. Extrusion temperature during the process varied in a range from 360 to 470°C. Hot extrusion method scheme is shown in Fig. 1. Homogenizing annealing of extruded rods with length of 250 mm was performed at automated stand (AutoAF, RusTec) at temperature of 400°C.

Measurements of thermal EMF coefficient α, electrical conductivity σ were performed at multi-position automated stands (AutoMS, RusTec). Measurement of thermoelectric figure of merit ZT was performed using 4-wired

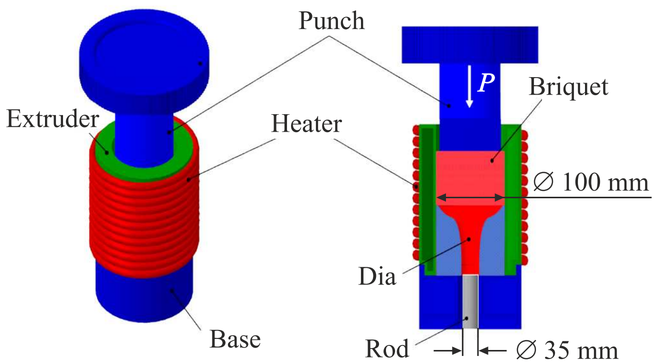

Figure 1. Hot extrusion method scheme.

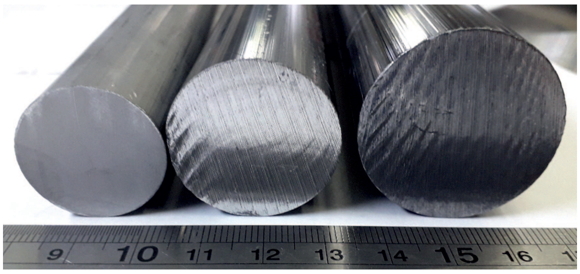

Figure 2. Extruded rods with diameter of 25, 30 and 35 mm.

Harman method [14]. Archimedean method was used for density measurement. Mechanical uniaxial compression tests were performed at universal testing machine „Instron“.

To examine the texture using X-ray diffractometry method the samples were cut from extruded rod perpendicular to extrusion axis. Inverse pole figures (IPF) building method was used for texture evaluation. IPF were built as per diffractograms, observed from cross sections, perpendicular to extrusion axis, i.e. the possibility of different plane poles match with extrusion axis was evaluated. Morphology of the extruded samples fracture surface was examined using scanning election microscope (HRSEM).

3. Discussion of results

Thermoelectric properties of extruded materials significantly depend on several process parameters, such as crystal drawing ratio and the follow-up annealing mode. Table includes thermoelectric parameters of materials based on Bi_2Te_3 of *n*- and *p*-type of conductivity at room temperature: coefficient of thermal EMF α, resistivity ρ, power factor (PF) α^2/ρ and thermoelectric efficiency

$$Z = \alpha^2/\rho\kappa, \tag{1}$$

where κ is the thermal conductivity of thermoelectric material.

The table shows that increase of thermoelectric efficiency Z of material is achieved by increasing the drawing ratio K due to great perfection of deformation texture.

Figure 2 shows the picture of extruded rods with various diameter based on Bi_2Te_3.

Figure 3 shows the picture of fracture surface in secondary electrons — raster electron microscopy (REM).

Significant differences in microstructure of samples of *n*- and *p*-type of conductivity are not observed. The average grain size after plastic deformation and follow-up annealing is $\sim 30\,\mu$m. In polycrystals of *p*-type at large magnification the intragranular microporosity with size from fractions to $1\,\mu$m is well-visible. Pores are of isotropic shape.

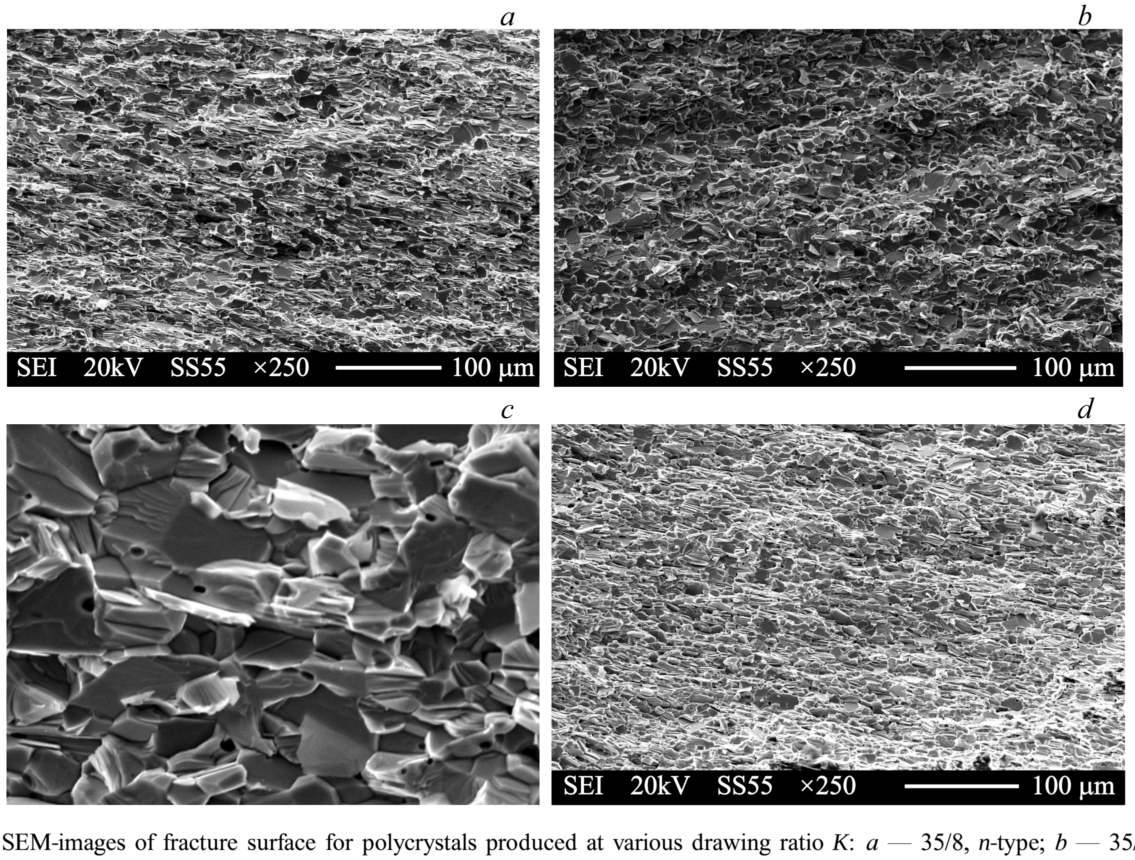

Figure 3. SEM-images of fracture surface for polycrystals produced at various drawing ratio *K*: *a* — 35/8, *n*-type; *b* — 35/11, *p*-type; *c* — magnified view of structure, *p*-type; *d* — 25/22, *p*-type.

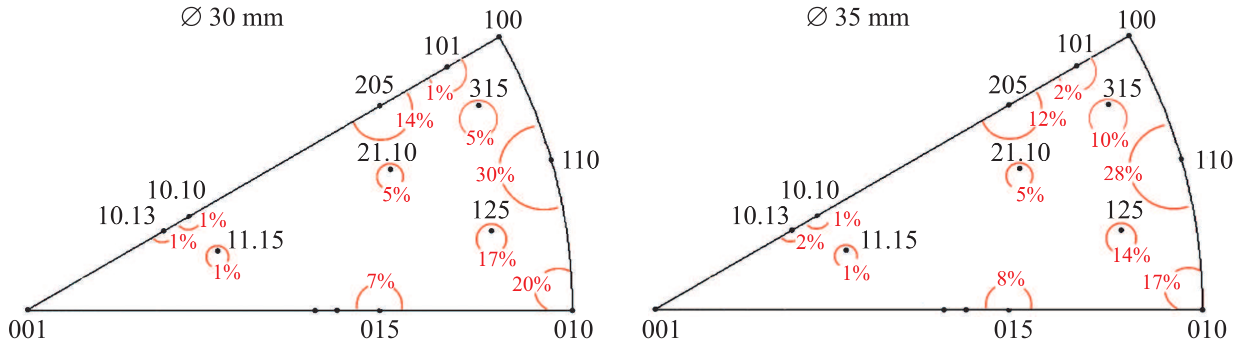

Figure 4. IPF for washer edge using the example of thermoelectric material of *n*-type of conductivity.

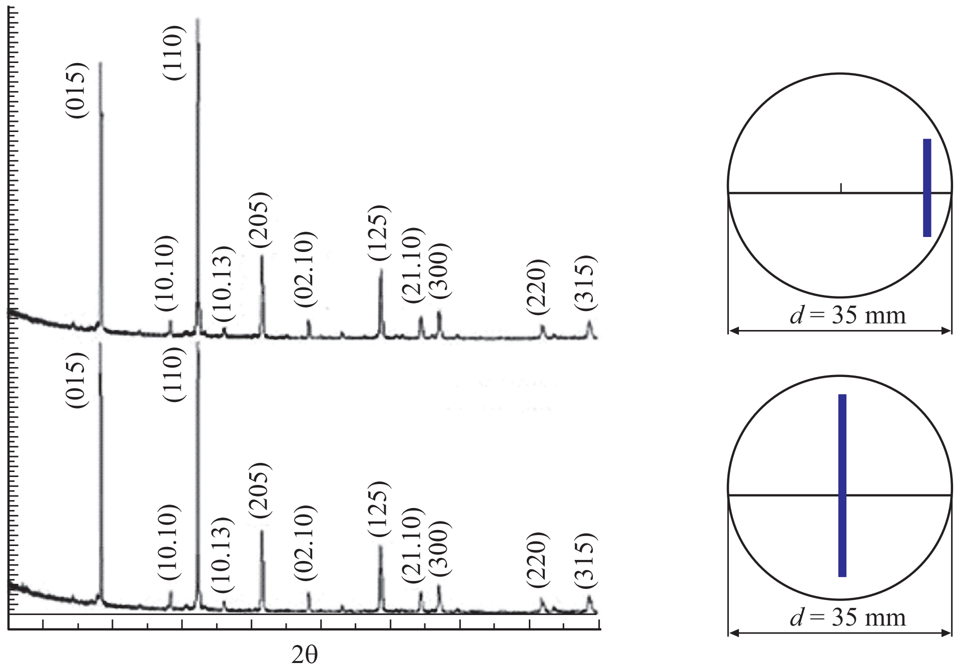

Figure 5. Diffraction line intensity variation for extruded rods of *p*-type with diameter $d = 35$ mm.

To examine the texture, forming during extrusion, the samples were cut from extruded rod perpendicular to extrusion axis. Inverse pole figures (IPF) building method was used for texture evaluation. IPF were built as per diffractograms, observed from cross section, perpendicular to extrusion axis, i.e. the possibility of different plane poles match with extrusion axis was evaluated.

Plastic flow increases in the middle of a rod, closer to extrusion axis. At extruder exit the deformation texture is formed, primarily (110) and (100), while the area axis is parallel to extrusion axis. At the same time the cleavage planes are also located along extrusion axis. Figure 4 shows texture variation as per IPF charts for material of *n*-type of conductivity at transition from extruded polycrystal diameter of 30 to diameter of 35 mm.

IPF of the central part of washer, built as per diffractograms of the examined rods of various diameter, are almost the same. The common trend of insignificant weakening of texture on a rod edge is observed. Over the length of extruded rods the texture is almost the same.

Figure 5 shows diffractograms, made from a washer of extruded material of *p*-type of conductivity with diameter of 35 mm, cut perpendicular to extrusion axis from the central part of the rod.

Variation between center and periphery at drawing ratio $K = 8$ is 4%. At drawing ratio increase to 11 in material of *p*-type of conductivity, the discontinuity of tensile strength over cross section decreased to 1.5%. Thus, it is possible to achieve homogeneity of the structure and mechanical properties over cross section at diameter of 35 mm with the corresponding selection of drawing ratio.

This indicates the advantage of extrusion process for large-size rods, that can not be achieved using a method of direct recrystallization from melting.

Figure 6 shows dependence of tensile strength over cross section of extruded rods of *n*- and *p*-type of conductivity

Thermoelectric properties of extruded polycrystals based on Bi_2Te_3 of *n*- and *p*-type of conductivity at room temperature depending on drawing ratio *K*

Type of material	Diameter, mm/K	σ, MPa	α, μV/K	ρ, mOhm · cm	PF, 10^{-3}W · m^{-1} · K^{-2}	*Z*, 10^{-3} K^{-1}
n-Bi_2Te_3	25/16	230	203	0.953	4.30	2.92
n-Bi_2Te_3	30/11	210	203	0.952	4.33	2.85
n-Bi_2Te_3	35/8	180	203	0.966	4.29	2.83
p-Bi_2Te_3	25/22	200	211	0.981	4.54	3.26
p-Bi_2Te_3	30/15	180	207	0.966	4.47	3.24
p-Bi_2Te_3	35/11	180	208	0.962	4.47	3.23

with diameter of 35 mm. Samples were selected from the central part of the rod.

Figure 7 shows the dependence of tensile strength over the length of extruded rod. It shows that compressive tensile strength of rods of *n*-type with diameter of 30 and 35 mm with the same drawing ratio is on the same level.

Figure 8 shows the distribution of samples density over the rod length. During plastic deformation at extrusion of rods with diameter of 35 mm the densification of the examined material is observed. Macroporosity disappears and density reaches the theoretical values. Rods of *n*-type and *p*-type with diameter of 30 and 35 mm have similar density.

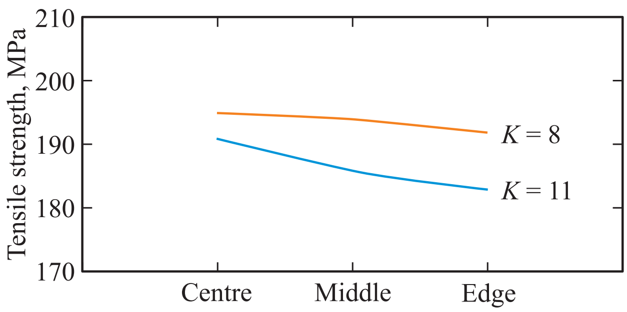

Figure 6. Tensile strength variation over cross section of sample of *n*-type ($K = 35/8$) and *p*-type ($K = 35/11$) with diameter of 35 mm.

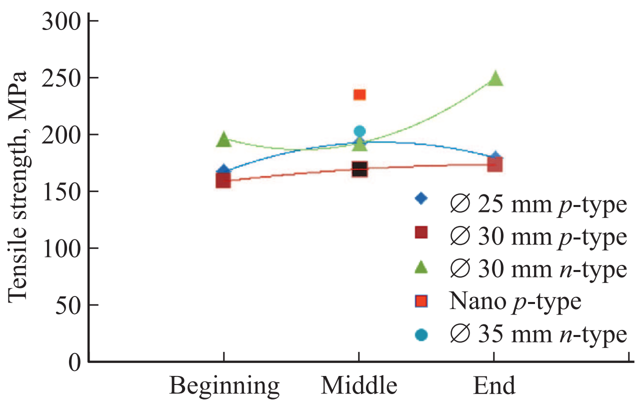

Figure 7. Tensile strength variation over the length of extruded rods.

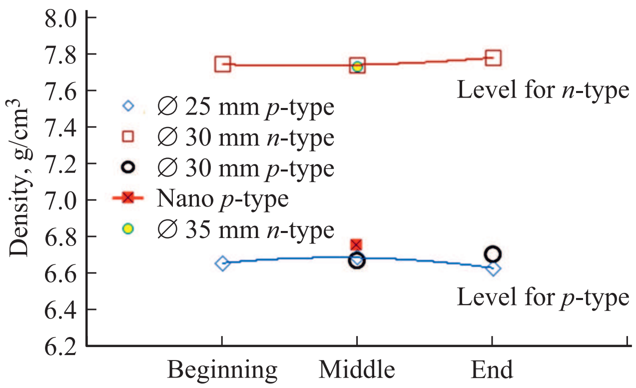

Figure 8. Distribution of samples density over the length of the rods of various diameters and for various types of materials.

Observance of optimum process conditions and extruder design allows to produce polycrystals with diameter of 35 mm, while providing the uniform deformation of polycrystal rod of thermoelectric material based on Bi_2Te_3 of *n*- and *p*-type of conductivity over cross section and length.

4. Conclusion

Technology of production of perfect polycrystals based on Bi_2Te_3 of *n*- and *p*-type of conductivity with diameter of up to 35 mm, homogeneous over the cross section and length, by means of hot extrusion method was developed for the first time ever.

Detailed examinations of structural properties of extruded polycrystals (deformation texture, grain size) were presented. Polycrystals mechanical properties (tensile strength) were studied.

Thermoelectric properties of polycrystal rods of various diameter (coefficient of thermal EMF, electric conductivity and thermoelectric figure of merit using Harman method) were measured. It was demonstrated that at certain drawing ratio the polycrystals based on Bi_2Te_3 of *n*- and *p*-type of conductivity with diameter of 35 mm, with almost the same thermoelectrical and mechanical properties as for regular size polycrystals (with diameter of 25 mm), currently commercially manufactured, were produced.

Funding

Structure study was performed using equipment of „Materials Science and Metallurgy“ Common Use Center with financial support of the Ministry of Education and Science of the Russian Federation (agreement No. 075-15-2021-696).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] N. Bomshtein, G.G. Spiridonov, Z. Dashevsky, Y. Gelbstein. J. Electron. Mater., **41**, 1546 (2012).
[2] L.V. Prokofieva, D.A. Pshenai-Severin, P.P. Konstantinov, A.A. Shaldin. Semiconductors, **43**, 973 (2009).
[3] P.P. Konstantinov, L.V. Prokofieva, M.I. Fedorov, D.A. Pshenai-Severin, Yu.I. Ravich, V.V. Kompaniets. Semiconductors, **39**, 1023 (2005).
[4] M.G. Lavrenteav, A.I. Sorokin, D.A. Pshenai-Severin, V.D. Blank, G.I. Pivivarov, V.T. Bublik, N.Yu. Tabachkov. J. Electron. Mater., **42**, 2110 (2013).
[5] A.P. Goncalves, C. Godart. *New Materials for Thermoelectric Applications: Theory and Experiment* (Springer, N. Y., 2013) p. 1.
[6] D.M. Rowe. *Thermoelectric Handbook: Macro to Nano* (CRC Press, Boca Raton, 2005).
[7] B.M. Gol'cman, V.A. Kudinov, I.A. Smirnov. *Poluprovodnikovye termoelektricheskie materialy na ocnove* Bi_2Te_3 (M., Nauka, 1972) (in Russian).
[8] Z. Dashevsky, S. Skipidarov. *Novel Thermoelectric materials and Device Design Concepts* (Springer, N. Y., 2019) p. 3.
[9] J. Herremans, B. Wiendliocha. *Aspect of Thermoelectricity* (CRS Press, Boca Raton, 2016) p. 39.
[10] O. Be*n*-Yehuda, R. Shuker, Y. Gelbstein, Z. Dashevsky, M.P. Dariel. J. Appl. Phys., **101**, 113707 (2007).
[11] R.A. Masut, C. Andre, D. Vasilevskiy, S. Turenne. J. Appl. Phys., **128**, 115106 (2020).
[12] M.G. Lavrentev, I.A. Drabkin, L.V. Ershova, M.P. Volkov. J. Electron. Mater., **49**, 2937 (2020).
[13] M.Maksymuk, T. Parashchuk, B. Dzundza, L. Nykyruy, L. Chernyak, Z. Dashevsky. J. Materials Today Energy, **21**, 100753 (2021).
[14] T.C. Harman. Appl. Phys. Lett., **129**, 1373 (1958).