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Development of multilayer thermoelectric modules based on bismuth telluride semiconductor

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One of the ways to increase the efficiency of thermoelectric generator modules (TE) is the use of multilayer TE dices composed of materials with maximum efficiency for various operating temperature intervals of the module. When creating multilayered dices, it is proposed to use the connection of separate sections (slice) by sintering the ultrafine powder of the silver. The powder is applied to the metallized surface of the slice of TE materials. A sandwich-type washer structure is formed, from which the dice of the TE module are then cut out. The resulting separation bound-ary between adjacent sections demonstrates high density (about 80% of bulk silver), good electrical and thermal conductivity (about 50% of bulk silver). The values of the tensile strength of multilayered dices are: 20 ± 8 MPa for *p*-type and 28 ± 10 MPa for *n*-type. The efficiency and cyclic reliability of samples of generator modules with multilayered TE dices were investigated. The studied module samples demonstrate a 10−12% increase in generation efficiency and higher cyclic reliability.

Keywords: hot extrusion, bismuth telluride, composite thermoelectric materials, multilayer thermoelectric element.

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1. Introduction

Today, great attention is paid globally to the development of alternative and, first of all, renewable energy sources [1–3]. An ideal solution would be at least a partial return of waste heat into the „energy system". One of the ways this waste heat can be used is its direct transformation into electricity by means of thermoelectric (TE) generators.

Therefore, TE modules improvement is in the spotlight today. To tackle this task two aspects are considered:

− development of efficient TE material;

− improvement of the module design to provide TE generator efficiency in whole.

TE material — is a key component of the module and it shall comply with the following requirements: high TE efficiency and outstanding mechanical properties.

Method of TE material extrusion became widely used in practice [4,5]. Among the benefits of the extrusion method are: outstanding mechanical properties along with high efficiency of extruded material; higher both, micro- and macro-homogeneity of transport properties compared to TE material obtained through melt growth.

TE materials based on bismuth tellurides and antimony tellurides have maximal efficiency in a quite limited temperature interval, therefore, in development of TE generators operating in a wide temperature range we need to use TE dices consisting of layers (slices) where current carriers density is optimal for their operating temperature [6].

This paper outlines an experimental technology of fabricating the multilayered dices and obtaining an improved version of TE generator module based on these dices.

2. Samples and study methods

The structure of powder and sintered material was studied by X-ray diffractometry method using Bruker D8 diffractometer ((Bruker AXS, Germany) and CuK_α-emission. The morphology of the sintered samples' cleaved surface in the mode of secondary electrons was observed with the scanning-electron microscope JSM−6480LV (JEOL, Japan). The surface profile was studied using Sneox (Sensofar, Spain) optical profilometer. The thermoelectric properties were measured using Harman method (RusTec, Russia). Generator modules characteristics were tested using TE generators test bench (RusTec, Russia). Digital laboratory adhesion tester (EASTONTECH, China) was used to check the strength of dices.

3. Material preparation

The thermoelectric material was fabricated by hot extrusion of a cold-pressed blank Bi_2Te_3 — Bi_2Se_3 (*n*-type) and Sb_2Te_3 — Bi_2Te_3 (*p*-type). The following initial components were used in the synthesis of solid solutions: tellurium, bismuth, antimony, selenium 99.999% pure by weight. Extruded rods 35 mm in diameter were fabricated.

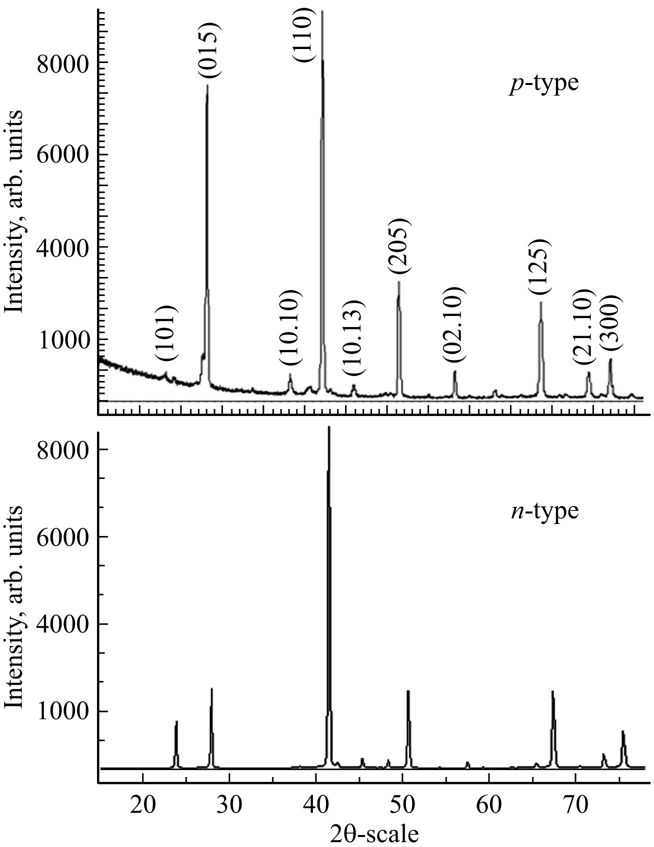

Figure 1. Area of diffraction pattern from the surface of extrusion normal axis.

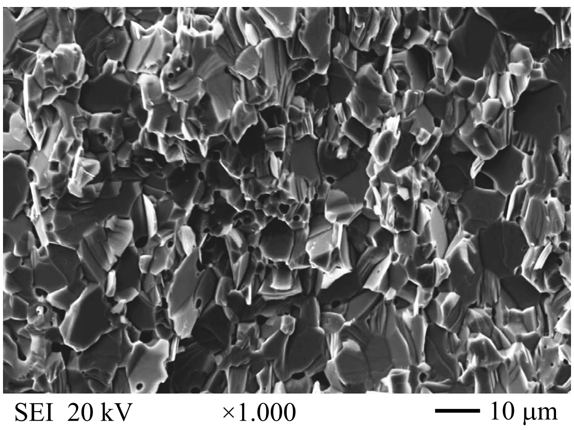

Figure 2. Image of cleaved surface of an extruded sample in secondary electrons.

Because extrusion is generally carried out at quite high temperatures, the structure of the extruded material is shaped during plastic deformation and dynamic annealing using several slip systems; this allows getting a deformation texture with primarily such a grain orientation where the grains cleavage planes are most probably oriented parallel to the extrusion axis (see Figure 1). The diffraction pattern shows about 5 reflections of grains the reflection planes of which are perpendicular to the rod squeezing axis during extrusion process. The structure major components are the grains with orientations [110] $\sim$ 73% that ensure the crystallographic anisotropy occurring in a favorable way (for *n*-type the anisotropy coefficient is 4–6 times) and reaching the maximal level of thermoelectric behavior in the thermoelectric module (TEM) extruded sample. The rest part of the ingot structure is occupied by less efficient grains with crystal-lattice orientations: [025] $\sim$ 11%, [215] $\sim$ 6%, as well as [105], [01.10] and other $\sim$ 10% in total. *p*-has slightly poorer structure, with higher percentage of grains disorientation. This is one of the root causes of poorer mechanical properties compared to *n*-type materials.

Materials obtained using this method are featuring good mechanical strength: at least 180 MPa compressive strength and at least 50 MPa bending strength. Extruded TE materials have high relative density, above 99.0%, and demonstrate high uniformity of stress-strain properties in both, cross-section and length of the ingots.

Figure 2 illustrates an image of the cleaved surface of *n*-type extruded sample in the scanning-electron microscope. The grain size of the polycrystalline structure is 6 μm in average. As observed from the structure of boundaries we may say that recrystallization was completed in the material. The redistribution of dislocations with formation of distinct grain boundaries is observed. Because of the small grain size as compared to the initial powder grain size (95 μm), it may be concluded that dynamic re-crystallization takes place during the extrusion process.

Figure 3 illustrates the results of measuring the temperature dependence of electrical conductivity (σ), and Figure 4 shows the results of measuring the thermoelectric efficiency (Z) within the temperature range 240–440 K for the extruded samples of *n*- and *p*-type. The measurements were accomplished using a 4-wire Harman method on $10.0 \times 10.0 \times 15$ mm samples. The specific feature of this method is that Z and σ are defined through direct measurements on one sample.

From the shown graphs of thermoelectric efficiency we may see that for the temperature range of 240–440 K there's no any optimal TE material based on solid solutions of bismuth and antimony chalcogenides.

At the temperatures of > 370–400 K the thermoelectric efficiency goes down (the value in this interval doesn't exceed $ZT = 0.8$). Therefore, component dices shall be used for the thermoelectric module to operate efficiently in this temperature interval. E. g., we may use one layer of material of the same base but with different level of alloying or of a composition with higher efficiency for a given temperature range.

3.1. Selection of material for TE generator modules

For fabrication of TE dices we used extruded materials with properties shown in Figures 3, 4. Material of *n*-dices operating at temperatures > 380 K: specific

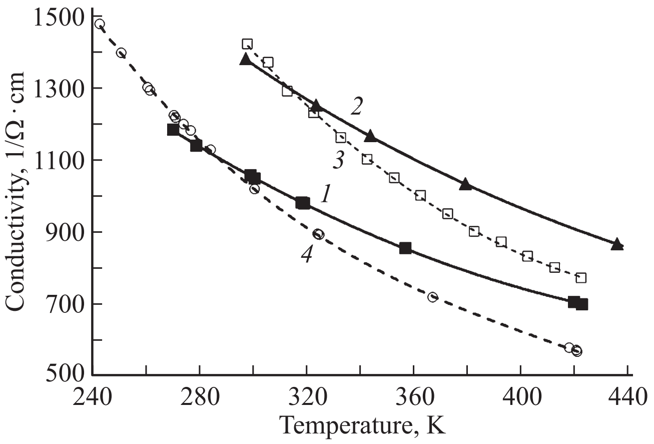

Figure 3. Temperature dependencies of electrical conductivity for the extruded samples of *n*- and *p*-type. Curves *1–4* indicate various alloying levels.

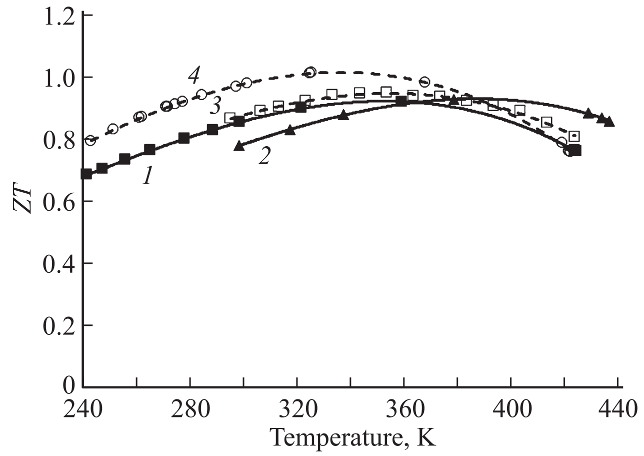

Figure 4. Temperature dependencies of efficiency for the extruded samples of *n*- and *p*-type. The designations are the same as in Figure 3.

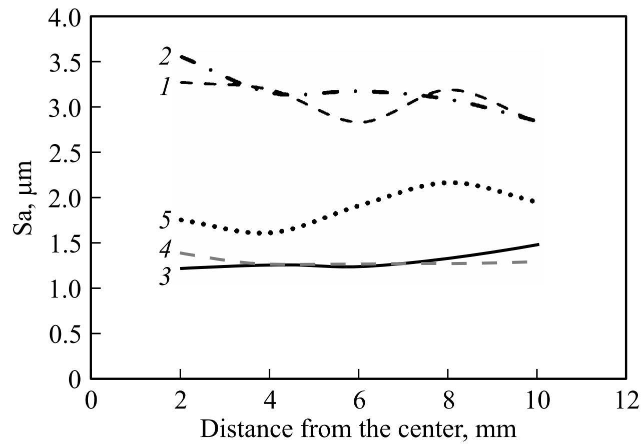

Figure 5. Mean arithmetic roughness of Sa surface versus distance from the center: *1* — super power mode, *2* — power mode, *3* — low power mode 100, *4* — low power mode 60, *5* — string cutting.

conductivity at 25°C $\sigma = 1380\,(\mathrm{Ohm \cdot cm})^{-1}$, composition $Bi_2Te_3 + 13\%Bi_2Se_3$. Height of disc $h = 1.08$ mm. Material of *n*-dices operating at temperatures < 380 K: specific conductivity 25°C $\sigma = 1050\,(\mathrm{Ohm \cdot cm})^{-1}$, composition $Bi_2Te_3 + 8\%Bi_2Se_3$. Height of disc $h = 0.42$ mm.

Material of *p*-dices operating at temperatures > 380 K: specific conductivity at 25°C $\sigma = 1410\,(\mathrm{Ohm \cdot cm})^{-1}$, composition $75\%Bi_2Te_3 + 25\%Sb_2Te_3$. Height of disc $h = 1.08$ mm. Material of *p*-dices operating at temperatures < 380 K: specific conductivity at 25°C $\sigma = 1040\,(\mathrm{Ohm \cdot cm})^{-1}$, composition $80\%Bi_2Te_3 +$ $+22\%Sb_2Te_3$. Height of disc $h = 0.42$ mm.

The layer heights of TE dices of *n*- and *p*-type were selected proportionately to the range of operating temperatures, i. e. from the ratio (380–340) K/(480–380) K the following was selected: height $h_1 = 0.42$ mm for the layer of TE material 1 with conductivity (1040–1050) $(\mathrm{Ohm \cdot cm})^{-1}$; height $h_2 = 1.08$ mm for the layer of TE material 2 with conductivity (1380–1410) $(\mathrm{Ohm \cdot cm})^{-1}$.

Individual layers were fabricated by cutting the ingots of *n*- and *p*-type ∅35 mm on the electro-spark discharge machines. Condition of TEM surface significantly impacts the contacts characteristics. It was found that if the process mode of electric spark cutting of TE material was selected correctly this will provide the best surface microrelief value and the material homogeneity in the cross-section. A rough surface with sharp peaks and troughs gives rise to coatings deformation. If the TEM surface roughness is commensurate with the coating thickness, the coating may be disrupted. This has a negative effect on adhesion and contributes to an increase in electric resistance of contacts. Lower microrelief decreases the probability of disruption of the anti-diffusion layer — semiconductor contact area and provides maximal adhesion of over $1.8\,\mathrm{kg/mm^2}$.

Figure 5 shows the findings of the surface microrelief study for the above-mentioned type of cutting. Conventional string cutting method is given for comparison.

By improving the cutting conditions we obtained the best surface profile of the plates in cross-section (mode *4* in Figure 5). It should be noted that conventional string cutting is distinguished by higher inhomogeneity in the cross-section (curve *5* in Figure 5).

After fabrication of TE material discs of specific thickness by method of electro-spark cutting (mode *4*) the discs were chemically treated followed by application of a functional anti-diffusion nickel coating in several steps with a total thickness of 10–15 μm and an interconnect layer (immersion gold 0.1–0.2 μm thick) (Figure 6).

To obtain the diffusion bonding of metallic gold-coated discs of TE material the silver nano-powder (Ag) films 65–80 μm thick on a polymer substrate Argomax® 8020 were used manufactured by ALPHA®.

The bonding itself was carried out in a vacuum chamber. The size of silver nano-powder was 20–40 nm. Every particle of Ag is encapsulated in an organic shell which evaporates during heating. Such powders can be treated

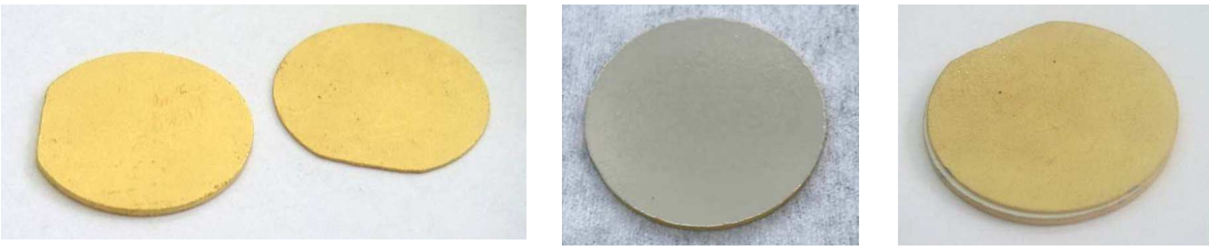

Figure 6. Sequence of operations in fabrication of multi-layered discs: *a* — TE material discs 1.08 and 0.42 mm high after chemical treatment with application of anti-diffusion coating and interconnect layer of gold; *b* — disc after increment of an ultrafine silver powder from a polymer film; *c* — multi-layered disc after diffusion bonding using Argomax® 8020 film.

at temperatures of 190−00°C and low pressure to obtain the silver interface with a density up to 85%. After such treatment the film acts like a bulk silver with fusion point 962°C. The interface thermal conductivity — 200−300 W/mK, electrical resistivity — 2.5−3.5 μOhm · cm. Intermetallic phases are absent.

Through a series of experiments the following mode of diffusion bonding was selected: pressure — 5−6 MPa, temperature — 250−270°C, vacuum — 1 Pa. The depth of silver penetration in gold layer after diffusion bonding makes 5−10 nm.

TE dices from the multilayered discs were cut by electric-spark method at low power (see curve *4* in Figure 4).

№	*n*	Adhesion, MPa	*p*	Adhesion, MPa
1	*n*	26.3	*p*	22.3
2	*n*	35.2	*p*	25.2
3	*n*	28.4	*p*	19.4
4	*n*	29.6	*p*	19.6
5	*n*	27.6	*p*	18.2
6	*n*	33.2	*p*	22.3
7	*n*	31.1	*p*	21.3
8	*n*	28.6	*p*	20.3
9	*n*	28.3	*p*	19.6
10	*n*	27.5	*p*	19.2
Average		29.6		20.7

3.2. Mechanical testing of multilayer dices

The obtained multilayer dices were subjected to rupture tests. A tensile force was applied along the dices perpendicular to the plane of diffusion bonding. The dices were disrupted both, in metallization (layer of TE material contacting with metallization, this was especially relevant for *p*-type), and in contact surface of silver with gold. The test results are provided in the table below.

One of the causes of difference in mechanical properties of material of *n*- and *p*-type of conductivity is high plasticity of the latter. As a result with similar mechanical and chemical treatments the depth of disturbed layer in TE material of *p*-type is larger than that in TE material of *n*-type.

3.3. Efficiency of using multilayer dices

The obtained multilayer dices were used to fabricate the generator modules. The multilayer dices were placed in the assembly tooling in such a way that the dice section with high conductivity contacted with the substrate of the module's hot side. Sn-Cu-Ni brazing paste with a melt temperature of 227°C was used for fabrication of the module.

The properties of modules with multilayer dices were compared with properties of conventional modules with homogeneous dices. To fabricate the homogeneous dices TE material of 1 *n*-type and TE material of 1 *p*-type were used (Figures 3 and 4).

During the modules testing in generator mode the temperature of the cold side was maintained 70 ± 5°C, and the temperature of the hot side was 190 ± 5°C. All tests were made outdoors.

According to the findings, the generator modules with multilayer dices are featuring a noticeably higher efficiency of electric power generation (higher by 12−13% in maximum of the generated power).

3.4. Cyclic serviceability of modules with multilayer dices

Cyclic serviceability was checked on a test bench allowing to provide high speed cycling of temperature of the module's hot side within the range40/90°C due to the use of Peltier effect. The period of one cycle 40/90/40°C was 40−50 s. At that, the temperature of the module's cold side was registered on radiator as 40−50°C.

5 modules with multilayer dices and 5 modules with homogeneous dices were tested. The latter were tested for comparison. It was found that the multilayer dices allow greatly improving the modules' cyclic serviceability.

Thus, modules with multilayer dices can withstand at least 120000 cycles at 40/90°C before destruction. Primarily dices of *p*-type at the interface of two layers are destructed.

For modules with homogeneous dices the number of cycles till destruction is from 50 000 to 90 000. In modules with homogeneous dices the module is destructed because of lamination of metal from the dice of *p*-type.

The burnout of a dice layer with high conductivity may occur because of destruction of the anti-diffusion layer along with high current (6 A) flowing through the module for a fast change of the module's hot side temperature due to Peltier effect.

4. Conclusion

Comparison of modules with homogeneous and improved multilayer dices indicates that it is possible to obtain higher efficiency of electrical generation process.

The use of an ultra-fine silver layer as an interconnect layer in diffusion bonding of two TE dices sections ensures connection of non-porous surfaces with low contact resistance and high thermal conductivity.

After diffusion bonding the ultra-fine silver behaves like a bulk silver with melting point of 962°C.

Among the shortages of this assembly option is high cost of the silver film, $\sim 0.3\$/\mathrm{cm}^2$.

An alternative to the diffusion bonding with the use of silver powder or silver-based films may be brazing with the use of intermetallic compounds like Sn-Cu. However, the brazing materials in this method (the so called preforms) have been developed not so long ago.

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Conflict of interest

The authors declare that they have no conflict of interest.

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