Hot Extruded $(Bi,Sb)_2(Te,Se)_3$ Alloys for Advanced Thermoelectric Modules

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Abstract

Bismuth telluride based alloys are extensively used for mass production of thermoelectric modules. Its thermoelectric figure of merit has not shown a significant improvement from the value of Z near 3.0×10^{-3} K^{-1} as obtained by various methods based on the solidification from the melt or by means of powder metallurgy and hot extrusion. However, this saturation does not imply a slow-down in the module-manufacturing sector, as today's modules for cooling and power generation become more powerful, smaller and stronger. Continued progress in the manufacturing area strongly depends on improvement of the mechanical properties of thermoelectric materials. In order to evaluate practical limits for module miniaturization, we have analyzed hot extruded $(Bi,Sb)_2(Te,Se)_3$ alloys by mechanical spectroscopy, aided with scanning electron microscopy observations. To further meet manufacturing challenges we also compared diamond blade and Electro Discharge Machining (EDM), which are frequently used for material cutting, in directions parallel and perpendicular to the extrusion axis. Comparably favorable results were obtained for cross sections as small as 100×100 μm^2, for leg lengths larger than 1 mm. State of the art modules have been manufactured by Thermix Ltd (Ukraine) with 1.27 mm long legs, with square sections of 210×210 μm^2 and 150×150 μm^2, using EDM. These advanced modules with the total number of legs in the range of 300-400 have great potential for power generation under small temperature difference conditions.

Modules feasibility confirmed the advantage of extruded $(Bi,Sb)_2(Te,Se)_3$ alloys for micro module manufacturing; however, grain size and porosity of the extruded alloy were found to pose limiting factors.

Introduction

Thermoelectric alloys produced by different technologies are always in competition in terms of material performance, mechanical properties, beneficial ingots geometry, and of course associated production costs. However, when the materials produced by different means reach the module manufacturing line, they are complementary to each other. Materials produced by directional solidification result in high thermoelectric performance, moderate mechanical properties and acceptable manufacturing cost. Hot pressed alloys show good mechanical properties, low manufacturing cost but lower performance. Extruded materials combine high performance with excellent mechanical properties, but do not always provide the most economical solution. Each material is especially suitable for a particular module design and/or system application. For example, even the conventionally grown alloys, which have been used successfully for a large number of different modules types, cannot be used for fabrication of micro modules.

In the present research we have studied the practical advantages and technical limits of hot extruded thermoelectric alloys for micro modules manufacturing.

Material Preparation

In this work, we have investigated extruded rods of N- and P-type $(Bi,Sb)_2(Te,Se)_3$ thermoelectric alloys with circular (25.4 mm diameter) cross-sections. The starting materials were bismuth antimony, selenium and tellurium shots of 99.999% purity. Mechanical alloying carried out the transformation of the pure elements into the required material composition. Powdered alloys were then extruded at a temperature between 400 and 500°C. Lengths of the extruded rods were in the range of 30-70 cm depending on the amount of powder used for extrusion. Further details of the material synthesis and doping were presented previously [1,2].

Material Properties

After hot extrusion, room temperature figures of merit of up to 3.3×10^{-3} K^{-1} for P-type alloys and 2.85×10^{-3} K^{-1} for N-type alloys have been obtained with optimized composition and charge carrier concentration. Typical variations of thermoelectric figure of merit as a function of temperature are presented in Figure 1 for N-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95},Se_{0.05})_3$ and P-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ alloys.

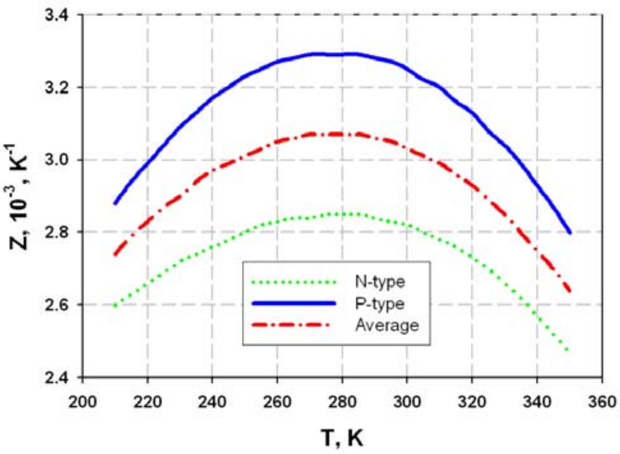

Figure 1: Variation of the thermoelectric figure of merit as a function of temperature for the N- and P-type rods.

Mechanical properties are especially important for micro module manufacturing. Scanning electron microscopy observations and X-rays diffraction of extruded alloys [1, 3-5] show grains of 10 to 20 µm in size preferentially oriented with the c-axis in a radial direction and perpendicular to the extrusion axis. Mechanical strengths as obtained by threepoints bending tests [4] are about two times stronger (70-100 MPa) when the bending force is applied in a direction perpendicular to the extrusion axis compared to the force applied parallel to the extrusion axis (40-60 MPa), where the lower values quoted to the P-type alloy. Variation of the elastic constants along the radial distance [6] shows a moderate increase of the texture near the rod surface. Using Mechanical Spectroscopy analysis [5,7,8] we found a strong correlation between Young's modulus and material density, which is presented in Figure 2.

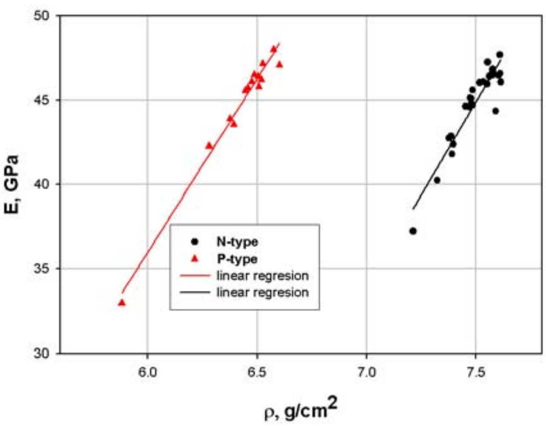

Figure 2: Variation of Young's modulus as a function of sample density for the N- and P-type rods.

We attributed this variation to the material porosity [5, 9]. Estimations based on material density measurements and scanning electron microscopy observations give porosity values up to 4% for practically usable extruded TE alloys. Porosity has only a marginal influence on the thermoelectric performance of studied alloys.

Material Cutting Experiments and Module Manufacturing

We have previously reported [10] the successful use of our extruded alloys for multistage modules manufacturing. Micro modules of 1, 2, 3 and 4 stages have demonstrated high thermoelectric performance. All modules were produced on the base of legs 0.6 x 0.6 mm^2 in section and 1 mm long. One-stage modules with legs length reduced down to 0.5 mm were also produced. Good mechanical properties of the extruded material have insured the neat shape of the legs and the module itself. Short-legged modules are beneficial for high heat density pumping.

For some applications like power generation under small temperature differences it is necessary to build modules with long and narrow legs. This is an extremely challenging task because of the generally weak mechanical properties of bismuth telluride based alloys. Electro discharge machining does not apply direct mechanical stress on the working material. Therefore we have tested EDM cutting for micro modules part manufacturing. A molybdenum wire of 60 µm in diameter was used, with a 20 µm precision on wire positioning and a 2 mm/min wire displacement velocity. Legs 1.27 mm long, with square sections of 210×210 µm^2 and 150×150 µm^2 were successfully cut from Ni plated wafers using EDM. Figures 3(a) and (b) show scanning electron microscopy images of the N- and P- types legs with 150×150 µm^2 square sections. Good quality of soldering alloy wetting of the leg end can be clearly seen under 500 × -magnification in Figure 3(b). This image also reveals some roundness of the leg edges. This is not surprising because the electric field is the highest at the edges and as a result EDM is more efficient.

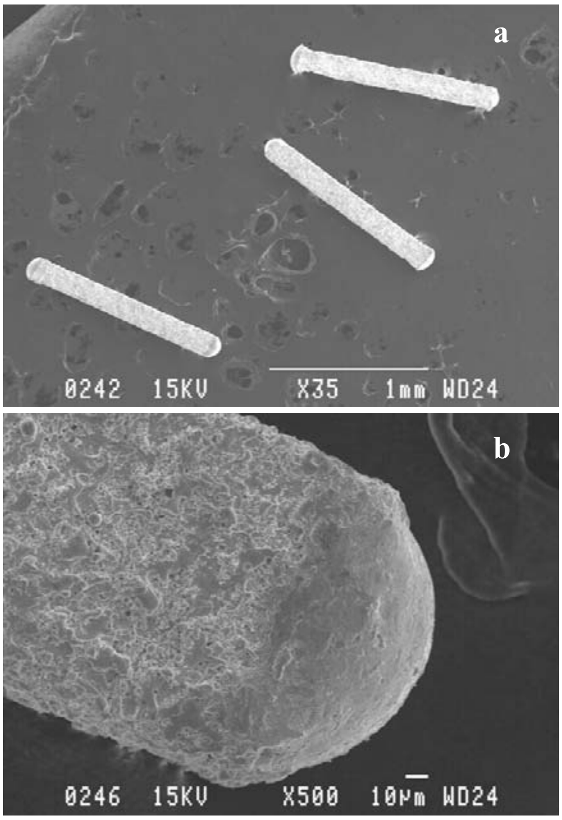

Figure 3: Scanning electron microscope observation of the legs with square sections of 150×150 µm^2 cut by EDM from the N- and P-type rods (a) and leg end with Ni coating and soldering alloy wetting (b).

An EDM alternative for legs manufacturing is diamond blade cutting using a dicing saw. We have used a RFK 775 dicing saw from Diamond Touch Technology Inc which allows a precision in blade positioning of 0.5-1 µm. By using a 400 µm thick blade, spindle rotation of 8000 and 16000 rpm and blade feed rate of 0.5 mm/s, we succeeded in cutting 1 mm long legs with square sections of 200×200 µm^2, 150×150 µm^2 and 100×100 µm^2. The legs were cut from a previously Ni electroless coated 1 mm thick N- type wafer. Scanning electron microscope observations of the legs are presented in Figures 4(a) and (b). It can be clearly seen that diamond blade cutting insure neat legs shape with rectangular cross section. We have not observed any delaminating of the Ni coating at the 500 × -magnification (Figure 4(b)). However, initial cutting experiments performed on the P-type Ni plated wafer were negative. Nickel delamination largely occurred for leg cross-sections of 150×150 µm^2 and 100×100 µm^2. As we have mentioned earlier, P-type alloys are mechanically weaker than N-type alloys. In [4] we have reported the mechanical properties of the interface between nickel contact and extruded $(Bi,Sb)_2(Te,Se)_3$ alloys. We have found a high enough tensile strength of 19 MPa for P-type alloy, but this value has been obtained after a high temperature exposure resulting from soldering alloy wetting and soldering procedures.

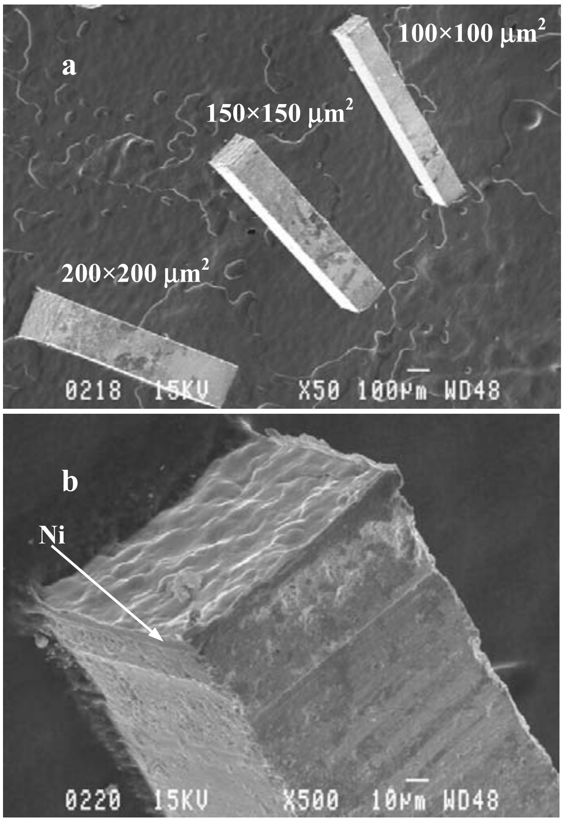

Figure 4: Scanning electron microscope observation of the 1 mm long legs with different square sections cut by diamond blade from the N-type Ni plated wafer (a) and 100×100 μm^2 leg end with Ni coating (b).

It is possible that interdiffusion through the contact interface increases Ni adhesion. In the present study we only tested diamond blade cutting of Ni plated P-type wafer with no additional heat treatment. Thus, more experiments searching for the right blade type, spindle rotation velocity, feed rate and lubricant are required.

We have so far discussed experiments focused on the manufacturing of freestanding legs. These legs are used in conventional module assembly lines. Modules of this type were assembled by Thermix Ltd (Ukraine) with legs 1.27 mm long and square sections of 210×210 μm^2 and 150×150 μm^2 cut by EDM. In Figure 5 we present the scanning electron microscope image of a module 6.7×8.2 mm^2 with 318 legs. The figure of merit for this module measured by the Harman method is 2.84×10^{-3} K^{-1} at room temperature. Module performance is coherent with the average P-N material performance shown in Figure 1 and a reasonable loss of Z value due to contact electrical resistance and ceramic plates' thermal resistance. Further details of performance and reliability are under study and will be reported elsewhere.

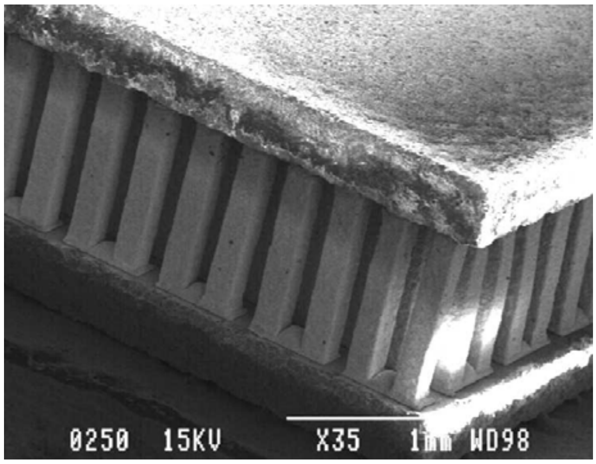

Figure 5: Scanning electron microscope observation of the micro module produced by Thermix Ltd (Ukraine) with legs 1.27 mm long and square sections of 210×210 μm^2 cut by EDM.

Material cutting by a dicing saw with a diamond blade may be beneficial not only in terms of precision attainable, but also because of the possibility of an integrated aproach to the module assembly. This process was described in [11] where miniature thermoelectric modules were manufactured using photolithography bump soldering and dicing.

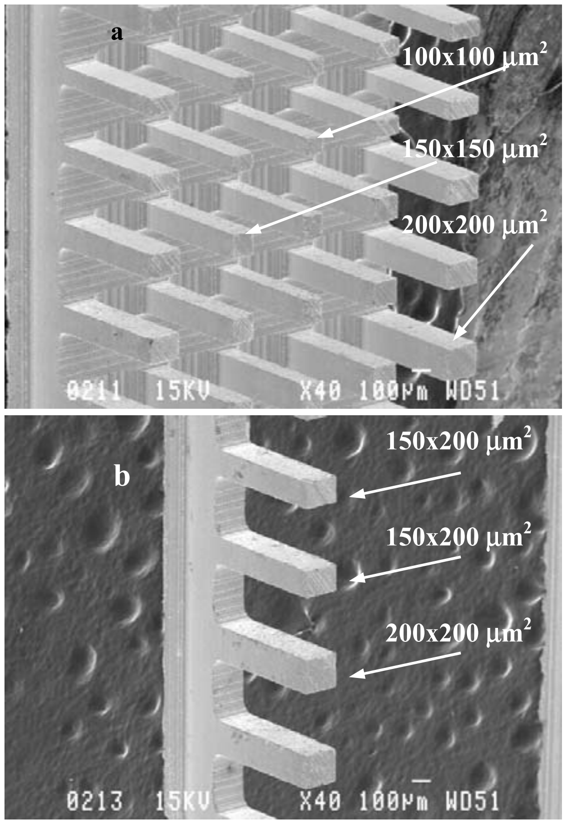

Figure 6: Scanning electron microscope images of N-type (a) and P-type (b) 1 mm thick wafers of extruded alloys after test cutting with a diamond blade.

We have performed prototype cutting in order to simulate integrated module manufacturing. In Figure 6, grids of legs of different square sections are presented. We used N- and P- type 1 mm thick wafers with no coating and the wafers were cut only on three quarter of their thickness to hold all pieces together. As the figure shows, both N- and P- type material can be equally cut with a diamond saw to provide miniature legs.

Conclusions

We have studied the practical and technical advantages and limitations of hot extruded thermoelectric alloys for micro modules manufacturing. We found that miniature legs can be successfully cut using EDM process or diamond blade dicing. Electro discharge machining is known to apply negligible stress to the working pieces. However, down from $150 \times 150\ \mu m^2$, roundness of leg edges becomes important. Experimental miniature modules were produced by Thermix Ltd (Ukraine) using EDM manufactured legs. Legs 1 mm long with square sections of $100 \times 100\ \mu m^2$, $150 \times 150\ \mu m^2$ and $200 \times 200\ \mu m^2$ were also produced using a diamond blade dicing saw. We have not found any deterioration of the legs shape, however, grains size of 10 to 20 µm leave small margin for further decrease of the legs section. Diamond blade dicing is beneficial for the development of an integrated approach to the module assembly.

Finally, the present study confirms that the manufacturing of advanced micro modules using hot extruded $(Bi,Sb)_2(Te,Se)_3$ alloys is practically possible and offers some advantages for integrated assembly.

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References

1. Simard J.-M., Vasilevskiy D., Bélanger F., L'Ecuyer J. and Turenne S., ″Production of Thermoelectric Materials by Mechanical Alloying – Extrusion Process″, Proc 20th Int. Conf. on Thermoelectrics, June 8-11, 2001, Beijing, China, pp. 132-135.
2. Simard J.-M., Vasilevskiy D., and Turenne S., ″Influence of Composition and Texture on the Thermoelectric and Mechanical Properties of Extruded $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ Alloys″, Proc 22nd Int. Conf. on Thermoelectrics, August 17-21, 2003, La Grand-Motte, France, pp. 13-18.
3. Vasilevskiy D., Simard J.-M., Bélanger F., Bernier F., Turenne S. and L'Ecuyer J., ″Texture Formation in Extruded Rods of $(Bi,Sb)_2(Te,Se)_3$ Thermoelectric Alloys″, Proc. 21th International Conference on Thermoelectrics, Long Beach, California, USA, August 2002, pp. 24-27.
4. Vasilevskiy D., Roy F., Renaud E., Masut R.A. and Turenne S., ″Mechanical Properties of the Interface between Nickel Contact and Extruded $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ Thermoelectric Materials ″, Proc 25th Int. Conf. on Thermoelectrics, August 6-10, 2006, Vienna, Austria, pp. 666-669.
5. Vasilevskiy D, Turenne S., Masut R.A., ″Application of Mechanical Spectroscopy to the Study of High Performance $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ Extruded Thermoelectric Alloys ″, Proc 26th Int. Conf. on Thermoelectrics, June 3-7, 2007, Jeju Island, Korea, in press.
6. Pelletier R., Turenne S., Moreau A., Vasilevskiy D, Masut R.A., ″Evolution of Mechanical Stresses in Extruded $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ Thermoelectric Alloys subjected to Thermal Shocks present in Module Fabrication Processes″, Proc 26th Int. Conf. on Thermoelectrics, June 3-7, 2007, Jeju Island, Korea, in press.
7. Golovin S.A., ″Methods of Mechanical Spectroscopy in Physical Metallurgy″, Metal Science and Heat Treatment, Vol. 44, Nos.5-6, 2002, pp.227-231.
8. Spinner S., Tefft W. E., ″A method for determining mechanical resonance frequencies and calculating elastic moduli from these frequencies″, Proceedings ASTM, Vol. 61, 1961, pp.1-14.
9. Phani K. K., ″Elastic-constant-porosity relations for polycrystalline thoria″, Journal of Material Science Letters, 5, 1986, pp. 747-750.
10. Vasilevskiy D., Semenyuk V., Turenne S., ″Properties of Cooling Modules Produced from $(Bi,Sb)_2(TeSe)_3$ Hot Extruded Alloys″, Proc 3rd European Conference on Thermoelectrics, Sept. 1-2, 2005, Nancy, France, pp.92-95.
11. Kishi M., Yoshida Y., Okano H and all, ″Fabrication of a miniature thermoelectric module with elements composed of sintered Bi-Te compounds″, Proc 16th Int. Conf. on Thermoelectrics, August 26-29, 1997, Dresden, Germany, pp. 653-656.