Thermoelectric Extruded Alloys for Module Manufacturing: 10 years of Development at École Polytechnique de Montréal

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Abstract

We review research carried out at the École Polytechnique de Montréal, over the past 10 years, on BiSbTeSe high thermoelectric performance materials. One practical result of this activity is a reliable powder metallurgy technology, combining mechanical alloying and hot extrusion to obtain P and N type polycrystalline alloys with enhanced mechanical properties. The extrusion process led to favourable crystalline texture resulting in thermoelectric figures of merit as high as 3.5 $\times 10^{-3}$ K^{-1} and 3.01 $\times 10^{-3}$ K^{-1} at room temperature for P- and N-type alloys respectively. Mechanical properties 2 to 3 times superior to those of conventionally grown material are confirmed by direct measurements and by manufacturing of advanced thermoelectric modules with very narrow or short legs. Results of extensive studies of transport phenomena, thermal, structural and mechanical properties, which were key factors to develop a deep understanding of this technology, are presented and discussed. An overview of the influence of composition and texture of extruded BiSbTeSe alloys on their thermoelectric (TE) and mechanical properties is also presented. Thermo-mechanical stresses in extruded materials and modules are analyzed with the help of finite element simulations and experimental validations. Some applications for these extruded high efficiency thermoelectric alloys are outlined.

1. Introduction

The hot extrusion process offers excellent prospects for the industrial production of Bi_2Te_3 based thermoelectric alloys. Materials produced by powder processing have greater mechanical strength and homogeneity when compared to conventionally grown alloys, leading to improved modules reliability. This is particularly important when the material will be exposed to elevated temperatures and high mechanical stress. These conditions are common for the hot side of thermoelectric generators (TEGs). In spite of the fact that for many waste heat recovery applications the temperature is in the range of only 100-200°C, when combined with mechanical stress, these conditions may lead to TEG failure. Nanostructured materials can offer higher thermoelectric performance [1], but are potentially less stable; mainly because of diffusion activated by thermo-mechanical stress fields which will tend to erase the pre-existing nanostructure. It is also important to note that large-scale waste heat recovery applications will require high thermoelectric materials consumption. Reducing the length of the module legs from 1.5 mm down to 0.5 mm leads to an increase of module specific power output by a significant factor of 9, which is equivalent to reducing the TE materials consumption by the same factor of 9. This leg shortening, however, is only possible when the TE materials can resist 3 times higher mechanical stresses.

2. Material Preparation

Through the last 10 years we have developed a reliable hot extrusion technology of bismuth telluride based alloys, as exemplified in Fig. 1.

Figure 1: Examples of bismuth telluride based alloys extruded in different shapes and size.

Circular rods (25.4 mm diameter) are the most convenient for modules manufacturing by combining optimized mechanical and thermoelectric properties with a large crosssection. They have been extensively studied and some key results are presented in this review.

Details of production from pure elements through room temperature mechanical alloying to hot extrusion are given elsewhere [2-4]. Precise control of the quantity of bismuth, antimony, selenium and tellurium shots of 99.999% purity leads to the formation of the $(Bi_{1-x},Sb_x)_2(Te_{1-y},Se_y)_3$ composition after a mechanical alloying process in an inert atmosphere. The formation of the alloy and the consequent disappearance of pure elements were confirmed by X-ray diffraction of the powder samples. Cold pressed billets of the powdered thermoelectric alloys were hot-extruded at a temperature between 400 and 500°C. We have examined extrusion temperatures ranging from 350°C to 520°C and extrusion pressures ranging from 120 to 760 MPa.

3. Texture and Mechanical Properties

When passing through the extrusion die, the extruded materials undergo a severe plastic deformation. The cleavage of the grains on the weak planes perpendicular to the crystallographic *c*-axis leads to a texture where the cleavage planes become aligned in the direction of the shear stress, parallel to the extrusion axis. Therefore the governing factor influencing the texture is related to the level of plastic deformation or to the equivalent plastic strain. The results of the numerical simulation by finite elements [3] show that the plastic strain is influenced by the extrusion ratio and the coefficient of friction between the bar and the die. On the other hand, the extrusion velocity does not modify the distribution of plastic strain along the bar. It is interesting to note that a reduction of the friction coefficient leads to a slight increase of the steady-state plastic strain regime and an increase of this regime results in a more homogeneous deformation.

Scanning electron microscopy of the surfaces fractured in different directions, presented in Figure 2, clearly reveals the specific texture of extruded materials.

The texture of the extruded materials was also confirmed by X-ray diffraction, anisotropy of electrical resistivity measurements, and by the evaluation of the thermal expansion coefficient and flexural mechanical strengths in orthogonal directions [3,4].

Different operations required for module manufacturing such as cutting, metalization and brazing subject the TE materials to important temperature gradients that could lead to degradation by cracking.

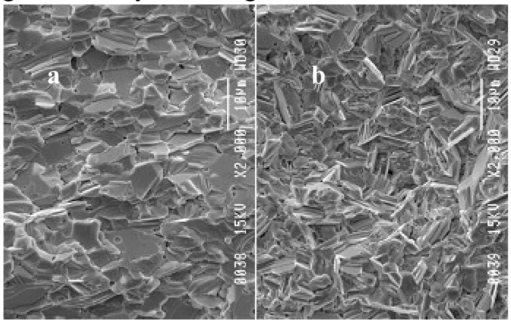

Figure 2: Scanning electron microscopy of the fracture surfaces (a) parallel to the extrusion axis and to the basal planes (b) perpendicular to the extrusion axis and to the basal planes.

To translate the effect of thermal gradient into mechanical stresses, it is necessary to evaluate the elastic constants in different orientations with respect to the geometry of the extruded rods and along the radius of the rod.

The compression and two shear sound velocities were measured in axial (ZZ), radial (rr) and tangential (θθ) directions using ultrasonic transducers [5].

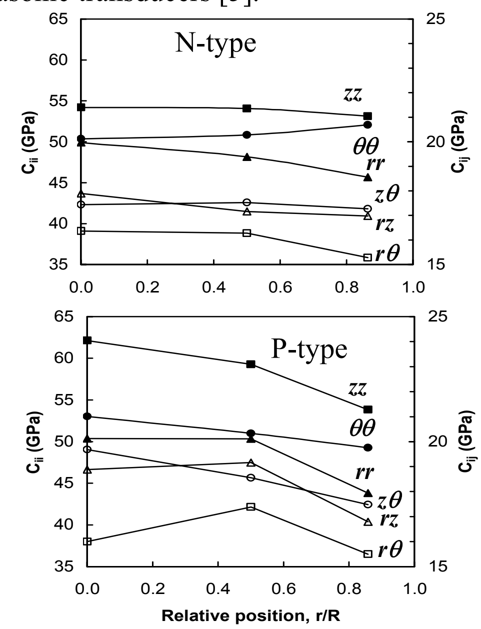

Figure 3: Variation of the elastic constants along the radial distance from the rods axis for N-type and P-type alloys.

The elastic constants C_{ij} defined by the particular geometry of the extruded specimens and along the radial distance from the rod axis are given in the graphs shown in Figure 3.

Spatial variations of the elastic constants caused by crystalline texture can be clearly observed. As previously characterized [3], the alignment of the weaker *c*-planes parallel to the extrusion axis and perpendicular to the radial axis of the rod becomes more important as we go from the center to the edge of the disc.

Specific texture in the extruded rods is a source of substantial stress remaining in the material even in a steady state when the temperature is homogeneous throughout the volume after any heating or cooling procedure. Stresses will remain in anisotropic materials because they originate from the difference of thermal expansion coefficients in the radial and tangential directions [2,5].

Local values of the elastic constants of the extruded materials were characterized using ultrasound frequencies. Important integrated information can also be obtained by analyzing audible frequencies corresponding to the fundamental longitudinal oscillations of full-length (30-90 cm) extruded rods. Mechanical spectroscopy analysis [6] revealed that the measured sound velocities are generally higher for P-type alloys (2600-2690 m/s) compared to those of the N-type alloys (2400-2500 m/s) and that they vary from one sample to another. We found a strong correlation between Young's modulus and the measured sample density, which is presented in Figure 4.

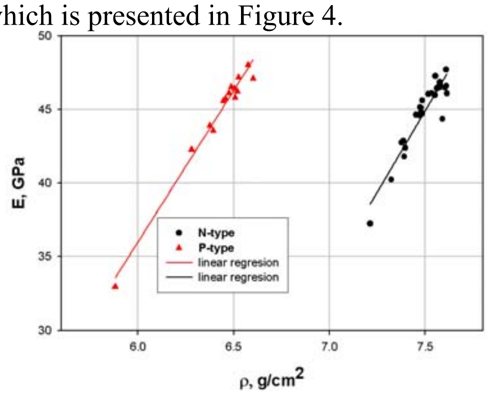

Figure 4: Variation of Young's modulus as a function of sample density for the N- and P-type rods.

We attribute this variation to the material porosity [6,]. Estimations based on material density measurements and scanning electron microscopy observations give porosity values up to 4% for practically usable extruded TE alloys.

The polycrystalline nature of the extruded material and its specific texture are the governing factors defining their mechanical properties. The grain boundaries act as a barrier to crack propagation and thus lead to a significant improvement in the mechanical properties. Compressive strengths of the order of 100 MPa were measured for both P- and N-type materials when stresses have been applied parallel to the extrusion axis.

4. Electrical transport phenomena

Study of electrical transport in extruded alloys is essential for thermoelectric materials. Figure 5 presents a 3D diagram showing the variation of the mobility μ of the electrons for different contents of Sb and Se at 77 K, 200 K and 300K.

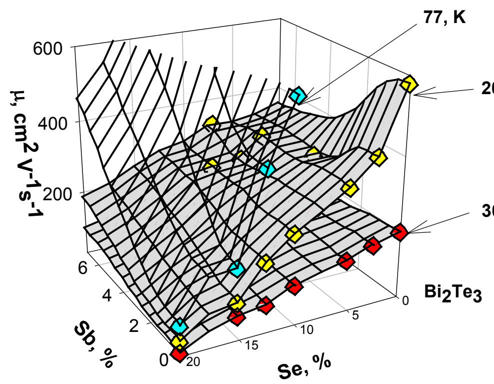

Figure 5: Carrier mobility μ as a function of Sb and Se compositions for three different temperatures. Dots represent experimental results.

The results show that maximum values of the electron mobility are obtained for pure Bi_2Te_3. An increase of the Sb and Se content leads to a reduction of electron mobility, which is in good agreement with the alloy scattering model.

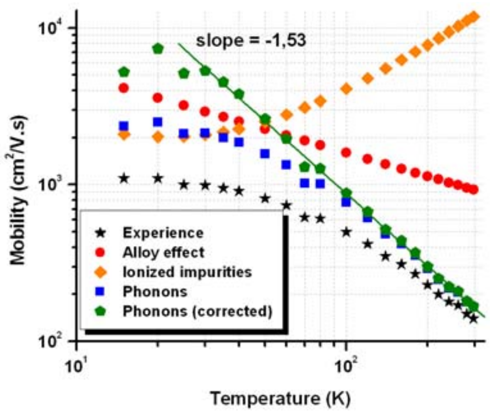

Figure 6: Extraction of electron mobility components as a function of temperature for $(Bi_{0,90}Sb_{0,10})_2(Te_{0,90}Se_{0,10})_3$ where $n = 1.9\times10^{19}$ cm^{-3}, $N_I = 7.9\times10^{19}$ ionized impurities cm^{-3}.

This phenomenon has been studied previously for the ternary system $Bi_2(Te_{1-y}\ Se_y)_3$ [7]. Analysis of the temperature variation of the electron mobility in the 15 - 300 K temperature range, presented in Figure 6, reveals screened ionized impurity, alloy and phonon scattering mechanisms.

An in-depth study [8,9] suggests the existence of complex anti-site defects, which contribute to the increase of the ionized impurity concentration. On the other hand we have not found any sign of scattering by grain boundaries. It is clear from our observations [6] that sample porosity can significantly modulate the elastic properties of extruded alloys. However, porosity has only a marginal influence on the performance of extruded TE alloys. We note that Z values tend to slightly increase with porosity, which is another sign of an intimate electrical inter grain contact in extruded materials.

5. Alloy Composition Optimization for Peltier Cooling Applications

The selection of optimal composition for P-type alloys is simple since it has been shown [10] that the alloy $(Bi_{0.2}Sb_{0.8})_2Te_3$ possesses an isotropic figure of merit Z even if the resistivity ρ, the heat conductivity λ and the Seebeck coefficient α are anisotropic. This remarkable behavior can be exploited advantageously in polycrystalline materials because the extrusion process causes only a limited preferential orientation of the grains in the extrusion direction. However, due to the isotropy of the figure of merit, extruded P-type alloys have figures of merit approaching those of conventionally grown alloys. Then the selection of the specific composition $(Bi_{0.2}Sb_{0.8})_2Te_3$ becomes an easy choice for the elaboration of P-type module components. The results obtained after hot extrusion of these alloys match perfectly well our predictions, with a figure of merit for the best specimens approaching 3.5×10^{-3} K^{-1}, which value is comparable to those reported for single crystals of the same composition.

The selection of chemical composition for N-type alloys is more complicated because the literature [10] and our results [3] confirm that the thermoelectric properties Z, ρ, λ and α show anisotropy. Given that each alloy production technology brings its own type of texture, the chemical composition of the alloys should then be adjusted to the specific technology to obtain optimal properties. The optimal composition is often determined empirically. Following the production method described previously, different alloys of the family $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$, were prepared with concentrations of Sb (x) varying from 0 to 10% and of Se (y) from 0 to 20%.

Figure 7 presents the variation of ZT at room temperature with the composition of the alloy resulting from interpolation between data points. The map shows a maximum ZT value of 0.88 for a composition of 5% Sb and 5% Se.

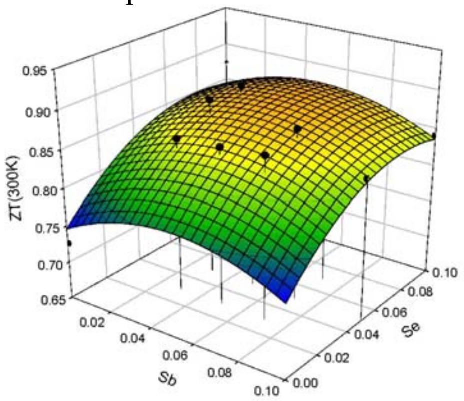

Figure 7: Variation of the figure of merit ZT at 300 K with the composition of the alloy $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$. Dots represent compositions evaluated experimentally.

6. Material Composition Optimization for TEG Application

N-type materials for TEGs present the same difficulties as for cooling modules and must be optimized by their composition. Generally, for heat recovery applications thermoelectric modules are exposed to a larger temperature difference ΔT compared to Peltier devices. Average $\overline{ZT}$ values calculated by integrating ZT over the desired temperature interval give the best parameter for the evaluation of material performance in larger ΔT. Figure 8 shows the variation of alloys performance with composition in the temperature interval 300-420 K.

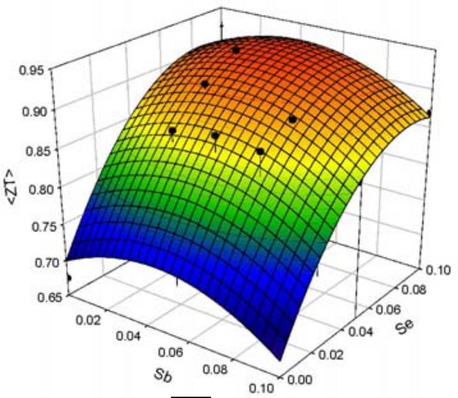

Figure 8: Average $\overline{ZT}$ for the 300-420 K temperature interval as a function of $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ alloy composition.

Comparing figures 7 and 8 we can see that variations of ZT with alloy composition are more pronounced at higher temperatures and the maximum performance of 0.93 has been obtained for x = 0.03 and y = 0.07.

Despite the loss of electron mobility (see Fig. 5), a gain in performance for quaternary alloys can be achieved by decreasing the lattice thermal conductivity.

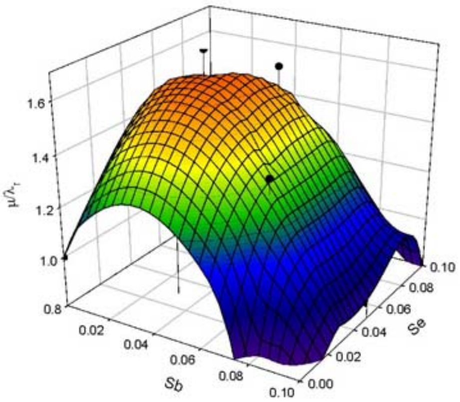

Figure 9: Normalized μ/λ_L ratio for the 420 K as a function of $(Bi_{1-x}Sb_x)_2$ $(Te_{1-y}Se_y)_3$ alloy composition.

Lattice thermal conductivities (λ_L) were calculated using measured total thermal conductivities, electrical conductivities and the Wiedemann- Franz law.

Variations of the μ/λ_L ratio (normalized by the value of this parameter for pure Bi_2Te_3) with alloys compositions are presented in Figure 9 and clearly show where phonon alloy scattering dominates over electron alloy scattering and where the combined effect of the introduction of Sb and Se is positive.

7. Thermoelectric Modules Produced from Extruded Alloys

One of the advantages of extruded materials is their superior mechanical strength. Miniature module legs with well-defined shape can be manufactured using Electro Discharge Machining (EDM) from this stronger extruded material. We also performed prototype diamond blade cutting in order to simulate integrated module manufacturing. In Figure 10, grids of legs of different square sections are presented. Both N- and P- type material can be equally cut with a diamond saw to provide miniature legs, however, grains size of 10 to 20 μm leave small margin for further decrease of the legs section.

Superior mechanical strength is not only a key factor for manufacturing operations but also favors module reliability under operating conditions with large temperature gradient. Reducing the length of the module legs from 1.5 mm down to 0.5 mm increases the mechanical stress by a factor of 3. Yet, modules with 0.5 mm legs have been successfully obtained using extruded materials.

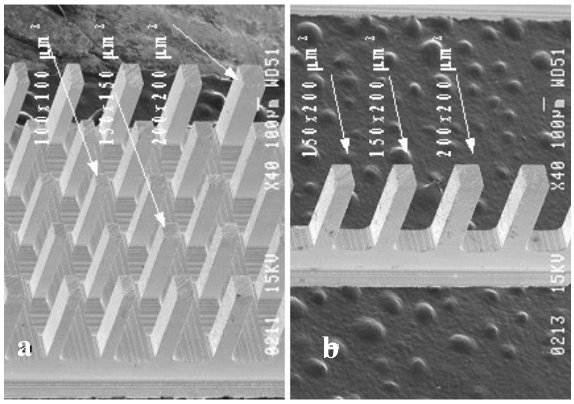

Figure 10 Scanning electron microscope images of N-type (a) and P-type (b) 1 mm thick wafers of extruded alloys after test cutting with a diamond blade.

Extruded materials combine enhanced mechanical properties with optimized thermoelectric performance as demonstrated by a series of cooling micromodules based on our extruded materials [11]. The maximum temperature differences of 76.4 K, 98.4 K, 115 K and 130 K have been respectively obtained for 1-, 2-, 3- and 4-stages TE modules.

State of the art modules with 1.27 mm long legs, with square sections of 150×150 μm^2, have also been manufactured. These advanced modules with the total number of legs in the range of 400 have great potential for power generation under small temperature difference conditions.

8. Conclusions

Through the last 10 years a reliable hot extrusion technology of bismuth telluride based alloys has been developed at the École Polytechnique de Montréal. Mechanically strong extruded materials with high thermoelectric figures of merit for optimized alloy compositions show many practical and technical advantages for applications. We highlight in particular that advanced bismuth telluride based thermoelectric micromodules with very narrow or short legs can only be manufactured using polycristalline extruded material. Micromodules with short legs demonstrate high cooling power density needed for spot cooling. TEG modules with narrow legs provide enough power for wearable wireless smart sensors using body heat of humans or other living beings.

Waste heat recovery offers a large-scale application for hot extruded $(Bi,Sb)_2(Te,Se)_3$ alloys. Reducing the length of the module legs down to 0.5 mm, which today is only possible using extruded materials, leads to a significant increase of module specific power output and as a result to a remarkable reduction of TE materials consumption. It is important to emphasize that reduction in module cost is a key factor for large-scale waste heat recovery applications.

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