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# Mechanical properties of bismuth telluride based alloys with embedded $MoS_2$ nano-particles

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ABSTRACT

We present a comprehensive study of the mechanical properties of bismuth telluride based nanocomposites containing $MoS_2$ nano-particles, obtained by mechanical alloying and hot extrusion. The addition of $MoS_2$ nano-particles significantly altered the crystallographic texture of the nanocomposites. Micro- and nano-structure analyses showed a drastic grain size reduction compared to that of conventional single-phase alloys. The nanocomposites improved their hardness and flexural strength by about 60% compared with the $MoS_2$-free samples. The calculated rupture energy showed that more than 100% higher energy for crack propagation is required at a content of 2.5 vol.% $MoS_2$ compared to not reinforced samples. The changes in the flexural elastic modulus may be partially explained by the alteration of texture. The observed enhancement in the mechanical strength and fracture toughness of nanocomposites can be attributed to grain refinement and to residual stress fields induced in the matrix by the introduction of $MoS_2$ nano-particles.



## 1. Introduction

Thermoelectric (TE) materials, since they can directly convert thermal energy to electrical energy and vice versa, have shown great potential for applications such as thermal sensing, solid state refrigeration/cooling, and power generation [1–3]. These materials that are generally brittle in nature possess low fracture toughness [4]. The mechanical properties are important in TE materials since poor performance leads to more material waste during device manufacturing, and consequently, higher cost of manufacturing. Also, mechanical performance is important in field applications in order to avoid TE device failure. In particular, TE generators in use are exposed to multiple causes of stress, such as thermal expansion mismatch between the materials, and externally applied forces or vibrations [5].

Bismuth telluride based alloys are known to be the TE materials of choice for applications near room temperature [6]. These alloys show remarkable anisotropy, which is due to their unique rhombohedral crystal structure, and which significantly influences their properties. The maximum TE performance of bismuth telluride based alloys have been found along the direction perpendicular to the *c*-axis of their crystals [7]. Although the single crystalline or unidirectional solidified bismuth telluride shows excellent TE properties, the ingots produced by this approach exhibit poor mechanical strength due to their coarse grains and weak van der Waals bonding between Te(1)—Te(1) layers (See Ref. [8]). The powder metallurgy approach has been employed to prepare polycrystalline bulk $Bi_2Te_3$-based alloys in order to improve their mechanical properties [9]. To maintain the optimum texture in the polycrystalline bulk $Bi_2Te_3$-based alloys and obtain the best TE properties, hot extrusion has been proposed to be one of the most effective consolidation technique [10].

Recently, there have been extensive numbers of reports on composite TE materials to enhance their TE performance mostly by reducing the thermal conductivity [11–15]. In contrast, the number of published papers discussing the mechanical properties of nanocomposite TE materials is very limited.

In the present work, we have investigated the mechanical properties of single phase bismuth telluride based alloy and its nanocomposites with embedded $MoS_2$ nano-particles as well as the effect of addition of $MoS_2$ nano-particles on the texture of these materials. We quantify how the addition of $MoS_2$ changes the texture of the nanocomposites, and we demonstrate a significant enhancement in their flexural strength and hardness with respect to conventional alloys. We have also studied the TE properties of these nanocomposites and detailed results including related discussions can be found in ref. [16]. The enhancement of the mechanical performance does not come at the expense of the TE properties, although there is still need of further optimization of the later.

## 2. Experiments

$(Bi_{0.2}Sb_{0.8})_2Te_3$ alloy powders were synthesized by mechanical alloying and then 0.2, 0.4, and 0.8 wt.%, (approximately 1.25, 2.5, and 5 vol.% in the bulk) amounts of $MoS_2$ nano-particles smaller than

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90 nm were added and mixed in an attritor. The mixed powders of each batch were hot extruded to obtain fully dense textured polycrystalline rods with 2.54 cm diameter and 30 cm length. The detailed description of the synthesis procedure has been published elsewhere [16,17].

To evaluate the mechanical properties of extruded alloys, we carried out flexural strength and microhardness tests. The flexural strength of the extruded alloy and nanocomposites was measured by a 3-point bending test using an Instron universal testing machine (Model 1123, Instron, Canton, MA) and a 500-N load cell. The test was implemented with a span of 40 mm, at a constant crosshead velocity of 0.5 mm/min, where the axis of applied force on the sample was perpendicular to the extrusion direction. The samples for flexural tests were prepared according to ASTM C1161-02c. Since the diameter of the extruded rods was smaller than the length of a standard specimen for a 3-point bending test, all samples were prepared along the rod as schematically illustrated in Fig. 1(a). The tests were repeated at least four times for each extrusion. The values quoted represent the mean value and the standard deviation obtained from the results of this set of repeated experiments for each extrusion.

Microhardness of the conventional single-phase alloy and of the nanocomposites was evaluated using a Buehler microhardness standard machine with an applied force of 100 gf (0.98 N) for indentation on the surfaces parallel to the extrusion direction. The presented hardness values for each samples, are the mean of fifteen measurements and the standard deviation of the obtained values are illustrated in form of error bars.

Generally, a material produced by powder metallurgy shows a density lower than its theoretical bulk density. This is mostly due to the porosity left in the sample as a result of imperfect sintering. We implemented the Archimedes method to measure densities of all the extrusions and investigated the densification of samples.

Study of the nanostructure and distribution of $MoS_2$ nano-particles in the matrix of nanocomposites was carried out using a JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM). Energy dispersive X-ray spectrometry (EDX) with convergent beam in this HRTEM was used for elemental composition analysis.

The microstructures of the nanocomposites were assessed by high-resolution scanning electron microscopy observations (HRSEM, JEOL JSM-7600 TFE). The average grain sizes of samples were calculated from the SEM micrographs by using ImageTools software. Accordingly, the reported average grain size in this work is defined by the diameter of circles with surface areas equal to the surface areas of grains observed in the micrographs. To calculate the average grain size that is representative of a whole sample, we take for each sample three SEM micrographs of three different magnifications from different places on etched surfaces of the samples. All grain sizes fall within a 30% spread around these average values. X-ray diffraction (XRD) measurements of these samples were carried out with a Philips X'Pert instrument (PANanalytical) with the sample surface (previously polished) perpendicular to the extrusion direction as illustrated in Fig. 1(b).

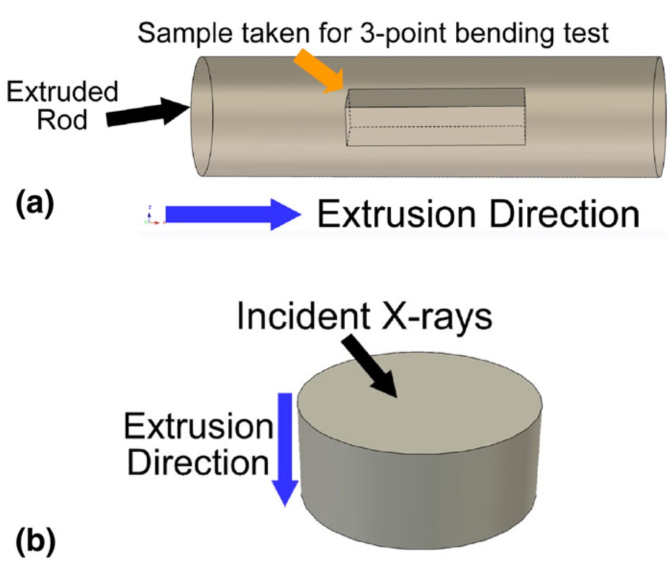


**Fig. 1.** (a) Schematic illustration of 3-point bending samples with respect to the extrusion direction, (b) schematic configuration of samples for XRD measurements.

We studied the degree of texture in our samples using their XRD patterns. The orientation degree ($F$) of a given crystallographic plane ($h'k'l'$) in the extruded rod can be calculated with the Lotgering method employing the following equation [18]:

$$F = \frac{\Pi - \Pi_0}{1 - \Pi_0} \qquad (1)$$

where $\Pi$ and $\Pi_0$ are the ratios of the integrated intensities of a specific plane ($h'k'l'$), denoted by $I(h'k'l')$, to those of all ($hkl$) planes for preferentially and randomly oriented samples, respectively, and can be calculated as follows:

$$\Pi = \frac{I(h'k'l')}{\sum I(hkl)} \qquad (2)$$

$$\Pi_0 = \frac{I_0(h'k'l')}{\sum I_0(hkl)} \qquad (3)$$

To obtain $\Pi_0$, XRD patterns of powders for each extrusion were taken prior to the extrusion and are considered as equivalent to randomly oriented samples. A perfectly oriented crystal has a $\Pi$ value approaching to 1 for a specific crystallographic plane, which is parallel to the sample surface; consequently, the $F$ value for that plane would be equal to 1. As the $F$ value of a given plane becomes closer to 1, the orientation of this plane becomes predominant for the chosen measurement configuration.

## 3. Results and discussion

In this section, first we will show results and discuss the effect of addition of $MoS_2$ nano-particles on the micro- and nano-structure of bismuth telluride based alloy. Then the texture of nanocomposites will be compared to that of the conventional single-phase alloy. Next we will present the results of mechanical properties including hardness, and flexural strength and discuss the strengthening mechanisms in our nanocomposites. The flexural elastic modulus as well as the rupture energy will also be presented and discussed. Finally, we will wrap up this section by discussing the relation of texture and elastic properties in our samples in addition to a brief overview of available works in the literature and comparison with the current study.

### *3.1. Micro- and nano-structural analysis*

The microstructural analysis of the single phase alloy and of the nanocomposites revealed significant grain refinement as the content of $MoS_2$ nano-particles increased in the specimens (Fig. 2(a–d)). Flake shaped $MoS_2$ nano-particles with lengths less than 20 nm and a few nanometers thickness were observed distributed in the bismuth telluride based matrix of the composites (Fig. 2(e)). The EDX analysis of sample areas having nano-inclusions (as selected in Fig. 2(e)) confirmed the presence of Mo and S in the nano-inclusions (see Fig. 2(f)). More TEM observations of these nanocomposites have already been published (See Ref. [17]). The grain growth suppression was clearly observed as it is illustrated in Fig. 2(a) to (d). This can be explained by a Zener pinning mechanism due to effect of nano-particles blocking