Study of plastic deformation and microstructure formation in bismuth telluride based thermoelectric materials during equal-channel angular pressing

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Abstract. This work is a complex experimental and theoretical study of the extrusion process by equal-channel angular pressing in the production of chalcogenides based on bismuth telluride, which are of interest for the creation of new functional thermoelectrics.

1. Introduction
A significant role in the analysis of equal-channel angular pressing (ECAP) is played by mathematical modeling [1,2], which allows describing the thermally stressed state of a sample during a plastic deformation in special geometry of ECAP (for example, for different angles and smoothing between channels etc.), in set conditions of thermal heating and for the set rate of the punch. The basis of the methodical approach is finite element method (FEM), implemented in commercial codes: ADINA, DEFORM, ABAQUS, MARC. Many studies are devoted to ECAP modeling in the production of high-quality aluminum alloys by using the elastic-plastic FEM model. The application of the elastic-viscoplastic model for the preparation of polymers is also considered. However, analogous studies of the ECAP process for the production of thermoelectrics (TE) based on bismuth telluride are absent. The theoretical approach is based on the mathematical model of the ECAP process using the elastic-plastic body approach. This model is supplemented by calculations of grain sizes, formed as a result of plastic deformation. Experimental studies were aimed at obtaining specific data on the distribution and size of grains in extruded materials, which are necessary for a verification of the mathematical model. A furnace for the production of TE materials based on solid solutions of chalcogenides was developed in the National University of Science and Technology (MISIS). Its functional diagram is shown in figure 1 a. The location of three channels with the angles of their rounded corners $\varphi_{12} = \varphi_{23}$, $\psi_{12} = \psi_{23}$ is shown in the plane $(x, y)$ of this drawing. Dimensions of the 1st channel: 2 cm in $x$ and 8.5 cm in $y$ directions; 2nd channel: 1.6 cm in $x$ and 1 cm in $y$; 3rd channel: 1 cm in $x$ and 3 cm in $y$. In the direction $z$, perpendicular to the plane of the drawing, the thickness of the channels and the initial sample is 2 cm. The essence of the ECAP process consist in pressing the initial powder through three
mutually perpendicular channels, which are located in a closed chamber heated to a predetermined temperature.

\[ \phi_{12} = \phi_{23}, \quad \psi_{12} = \psi_{23}; \quad q \rightarrow \text{heat flux from the heater.} \]

**Figure 1.** Press-die of the ECAP process (a): \( P \rightarrow \text{punch; the initial calculation grid for the sample in channel 1, channels 2 and 3 with the angles of rounded corners } \phi_{12} = \phi_{23}, \ \psi_{12} = \psi_{23}; \ q \rightarrow \text{heat flux from the heater.} \)

Calculation grid of the ECAP process (b). Vector image of plastic flow \((V_{\text{max}} = 0.028 \ \text{cm/s at } V_P = 0.018 \ \text{cm/s})\) at time \( t = 250 \ \text{s} \) (c).

2. The calculations of plastic deformation and grain formation

The methodical approach is based on the approximation of an elastic-plastic body. For the ECAP process, the thermal stresses may be neglected. The calculations were carried out by the FEM method using the \textit{MSC Marc}® code, where the equivalent plastic deformation \( \varepsilon \) is used as a quantitative characteristic of plastic deformation. The maximum value of \( \varepsilon \) was verified by using of the well-known analytical formula (1) from [2]. The transition of bismuth telluride from an elastic to a plastic state was experimentally determined: \( \sigma_c = 102 \ \text{MPa} \) is the critical stress. Other parameters are known from the literature data: \( E = 40 \ \text{GPa} \) is the Young's modulus, \( \nu = 0.3 \) is the Poisson's ratio. In this process, a graphite gasket is used to ensure the sample slipping along the die walls. Therefore, friction was not taken into account. The punch rate was set equal to \( V_p = 0.018 \ \text{cm/s} \). The process was modeled by taking into account the heating of the die and the sample to \( 420 \sim 515 \ \text{°C} \).

Calculations of the thermoplastic state of this material in the ECAP process were carried out using a moving FEM grid (figure 1 b), which during this process was adapted to the geometry of the die. The number of grid nodes was increased or decreased depending on the magnitude of plastic deformation for a satisfaction of the specified calculation accuracy and for the convergence of the iterative process. The calculated picture of plastic motion is illustrated by vector lines, which show its layered character (figure 1 c). The same layering nature of the extruded material can be seen on the longitudinal sections of the samples after the ECAP process. A detailed methodological approach to the calculation of grain sizes is presented in [3]. It is assumed that the initial grain size \( d_0 \) is set in the initial sample, and the formation of grains is limited by the magnitude of critical deformation, which is estimated as follows:

\[ \varepsilon_c = \alpha \exp\left(\frac{T_c}{T}\right). \]  

(1)
Here $\alpha = 4.76 \times 10^{-4}$, $T_C = 773 \text{ K}$. It is assumed that at $\varepsilon < \varepsilon_C$ the initial grain size is preserved. Otherwise, the grain size $d$ after recrystallization is calculated in depending on the strain rate and temperature according to the following formula:

$$d = \chi_1 \dot{\varepsilon}^{-\chi_2} \exp\left(-\frac{\chi_3 Q}{RT}\right).$$

(2)

Here: $\chi_1 = 11.3$, $\chi_2 = 0.14 \div 0.24$, $\chi_3 = 0.014$, and $Q = 267 \times 10^3 \text{ J/mol}$ is the activation energy of the formation of grains, $R = 8.314 \text{ J/mol K}$ is the universal gas constant.

The criterion for the transition to plasticity is the specified value of the von Mises stress. The analysis of the data in figure 2 a shows that in the 1st channel the sample moves straight from top to bottom and in initial contact with the 1st fillet the excess of the critical stress is insignificant. Therefore, small plastic deformations occur. However, after turning, the area of plastic deformations expands in the 2nd channel and is significantly strengthened in the entrance to the 3rd channel.

![Figure 2](image)

Figure 2. Contours of plastic deformation $\varepsilon$ at different times of the ECAP process at 470 °C: 70, 150 and 250 s (a); contours of grain sizes $d$ [µm] at $d_0 = 500$ µm, 470 °C, $t = 250$ s (b).

The magnitude of plastic deformation and its rate play a decisive role in the formation of the microstructure of the material. In particular, they determine the process of grain formation. Quantitative data on changes in plastic deformation during the process served as the basis for calculating the distributions and sizes of the formed grains in extruded sample. The contours of grain sizes in figure 2 b show that with small values of plastic deformation ($\varepsilon < 1$), the grain sizes are larger. Near the die rounding, the plastic deformation becomes significant ($\varepsilon > 1$), that causes the reduction of grain sizes to 10 µm. In this macro picture, the grain size ~ 20 µm is the predominant one, which is formed in the 1st channel and is determined by the parameters of the process.

3. The measured data

ECAP processes were carried out with different percentage composition of components and grain sizes of the initial powder. The design press-die was optimized and the experimental processes were carried out in different temperature modes to find the ways to control the microstructure, composition and defects in the extruded TE material. The microstructure of the samples was investigated by X-ray diffractometry, scanning and transmission electron microscopy (SEM and TEM), and their thermoelectric characteristics were measured by the Harman’s method [4]. Microstructure studies of the samples showed that their grains are fragmented, and the grain fragments themselves are separated by dislocation grids. It is noted that as the grain sizes of the initial powder increases, the volume density of dislocations decreases. The microstructure was studied by a scanning electron microscope.
for ECAP samples extruded for different grain sizes of the initial powder. The obtained TE material had a homogeneous and finely dispersed microstructure regardless of the different granule composition of the initial powders. The slots of the samples basically were as plates, which are characteristic for the layered structures of solid solutions.

Despite the different initial granule composition, after ECAP process the grain sizes in the slots of all samples did not exceed 5 µm. This is much smaller than the grain sizes of the initial powder. It is noted that with an increase in the grain size of the original powder, the texture improves, and the volume density of dislocations in the extruded material decreases. The largest number of grains with a favorable texture (from the point of view of electric anisotropy) is observed for samples with initial grain sizes that are ~ 500 µm. There are no grains with split planes that are parallel to the surface of the TE samples. The larger grain size of the original powder corresponds to the finer favorable texture. Thus, the anisotropy of the electric characteristics may be used in cutting the TE material as perpendicularly to the extrusion direction. TEM studies of the microstructure showed that within the grains there is a sufficiently high density of chaotically located dislocations (figure 3 a). The measured fraction of grains (%) of their size at an ECAP temperature 470 °C is shown in figure 3 b.

![Figure 3](image-url)

**Figure 3.** TEM image of the internal structure of grains with a resolution of 500 nm (a); measured grain fractions (%) upon grain sizes $d$ for the ECAP process at 470 °C (b); dependences of maximum grain sizes $d$ upon temperature $T$ (c): dashed line – measurements, solid line – calculations.

4. Conclusions
Measurement data became the basis for verifying the calculated grain sizes. A reduction of grain sizes with the increasing ECAP temperature is consistent with satisfactory accuracy with measurement data (figure 3 c). The increase in the discrepancy between the calculated and experimental data at higher temperatures (475 and 500 °C) may be explained by the lower compliance of the elastic-plastic model. The drawback of the model is its static nature, since the sizes and distribution of the grains are calculated at a specific time, using only the current values of plastic deformation.

Acknowledgments
This work was carried out in framework of IPMech RAS project No. AAAA-A17-117021310373-3 and at financial support by the RFBR (grants: 18-02-00036, 17-08-00078, 16-29-11785).

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