EXPERIMENT-CALCULATED STUDY ON STRUCTURE FORMATION OF THERMOELECTRIC MATERIAL BASED ON SOLID SOLUTIONS OF BISMUTH AND ANTIMONY CHALCOGENIDES PREPARED BY HOT EXTRUSION METHOD

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- *A mathematical model of hot extrusion process is proposed on which main the basic peculiarities of stress-strain state of prepared material are considered. A calculation model is based on the joint use of elastic-plastic body approximations. A numerical procedure employs finite-element approximation on the Lagrangian network which varies in time with a change in sample shape. Calculations were performed with the use of a set of Crystmo / Marc programs. By the example of thermoelectric composite* $Bi_{0.4}Sb_{1.6}Te_3$*, the evolution of stress-strained state of material was studied during different stages of extrusion process. The X-ray diffractometry, optical and electron microscopy techniques were used to study a change in the structure and texture along the extruded rod from a billet to extruder outlet. It was shown that the texture and microstructure of the extruded rod is formed under plastic strain in the region up to 4 cm from the upper edge of the die where the stresses are highest possible.*

Introduction

One of the main advantages of extruded Bi_2Te_3 based thermoelectric materials is a higher mechanical strength as compared to materials obtained by crystallization from the melt. Mechanical properties are of particular significance with the use of material in thermal generator modules and cooling micromodules.

As long as extrusion is generally carried out at rather high temperatures, the structure of extruded material is formed in the course of plastic strain which results in formation of strain texture. Extrusion conditions – die shape, strain temperature and velocity, strain value, initial billet structure – affect the final structure and properties of extruded material. One of efficient methods of studying the influence of these conditions on the formation of structure and texture of extruded material is mathematical simulation of extrusion process as combined with the experimental results of structural studies.

The necessity of mathematical simulation of extrusion stems from the following possibilities thereof:

- It allows determination of such process characteristics that cannot be established experimentally: the stress and strain fields and strain velocities not only at the final stage, but also their evolution during rod extrusion.
- Conducting virtual extrusion processes under different boundary conditions (particularly at different die constructions for given rod diameter) allows considerable reduction of the scope of works related to manufacture of expensive toolset.

Problem formulation and mathematical model

In the process of hot extrusion a cylinder billet pressed at room temperature from powder is extruded at temperature $T = 420$ °C through the die. The geometric parameters of the process were assigned: $D = 85$ mm – diameter and $L = 26$ mm – the length of initial billet, $\theta = 60°$ – die radius, $l = 10$ mm – length and $d = 20$ mm – diameter of cylinder part at outlet from the die. Punch travel velocity was also assigned: $V = 0.1$ mm/s. Extrusion ratio, determined by the relation D^2/d^2, characterizing the efficiency of hot extrusion process, in our case is 18.

Physical and mechanical parameters were selected according to data used in Ref. [1]: $E = 40$ GPa – Young's modulus, $\nu = 0.3$ – the Poisson coefficient. Critical stress of transition from elastic to plastic state at hot extrusion temperature $\sigma_0 = 102$ MPa was determined from the experimental "stress-strain" relationship that we established.

According to [1], the friction coefficient of sample and die f is 0.04. In the model, this friction is taken into account, but the calculations were performed ignoring it, since the hot extrusion process under study employs graphite grease assuring sample slipping.

In the work, a mathematical model is based on a joint use of elastic and plastic solid body approximations according to the basic concepts of elasticity and plasticity theory [2]. A detailed substantiation for the choice of this approximation is given in review [3].

Finite-element complex "Crystmo/Marc" was used for the simulation of hot extrusion process [4].

Simulation results

The elaborated mathematical model allowed carrying out virtual extrusion process which yielded an extruded rod of diameter 20 mm and length ~ 220 mm. In the course of calculation, the Lagrangian network and rod shape change as a function of time at different temporal steps of extrusion process, from which it follows that already in 150 seconds the rod starts leaving the die.

For the onset of rod leaving the die, Fig. 1 illustrates the basic zones of stress-strain sample state: 1 – high compression zone, 2 – structure formation zone and 3 – zone where longitudinal cracks may occur.

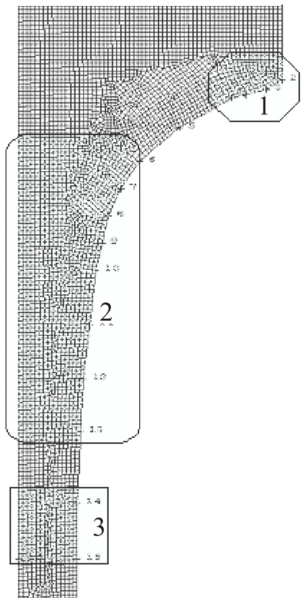

Fig. 1. Basic zones of stress-strain sample state: 1 – high compression, 2 – structure formation, 3 – zone where longitudinal cracks may occur.

From the distributions of isolines of plastic flow velocity V shown in Fig. 2 it is seen that at the beginning of the process ($t = 60$ s) the velocity is higher at the die wall. It is due to the fact that a more considerable contribution is from a lateral extrusion of material to the centre from zone 1 where compression is the largest. However, at the stage of rod leaving the die (*t* = 150 s) the radial profile of the flow changes in such a way that flow velocity in the centre becomes higher than that near the die wall.

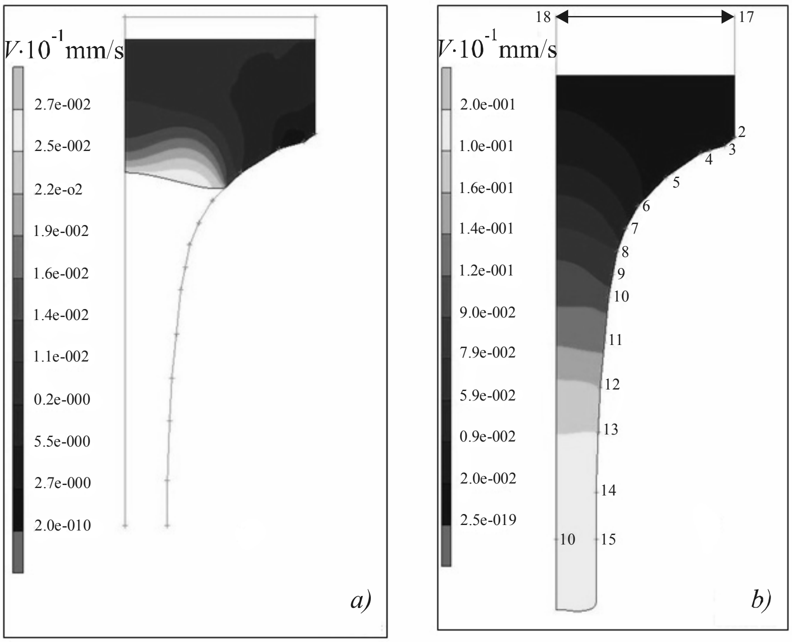

Fig. 2. Isolines of plastic flow velocity V: a – at the beginning of the process (t = 60 s): b – as the sample leaves the die (t = 150 s).

For further analysis of stress-strain state of the rod the most important is time moment (*t* = 150 s), corresponding to the onset of leaving the die by the rod.

Analysis of stress-strain state of the rod is done using the main maximum stresses σ and total maximum strains *s* occurring in the rod in the process of extrusion. Fig. 3 shows isolines σ and *s* as the rod leaves the die at *t* = 150 s. From the distribution of stresses it is seen that in the die throat from the lateral mark 2 to 11 their values are negative and change from –450 to –57 MPa, which corresponds to a drop in compression stress with distance from container. Then downward from mark 12 to 14 their values change their sign and the respective value of tensile stress reaches about 74 MPa. From mark 14 to 15 (on the cylinder portion of the die) and further from mark 15 (in a free sample) there is a radial inhomogeneity of stress: from 140 MPa of tension (on the die wall) to –57 MPa of compression (in the sample centre). Such radial inhomogeneity can cause the origination of longitudinal cracks when these values exceed the respective critical values.

From strain distribution it is seen that its largest value 4.5 is achieved at the angular point of the die (mark 2). From mark 3 to 10 there is a drop in strain value to 1.80. Between marks 10 – 13 one can see a wide zone of almost permanent strain 2.30. Downward from mark 13 (on the cylinder portion of the die) and then from mark 15 (in a free sample) one can see strain drop to 0.92. On this portion there is a radial inhomogeneity of strain corresponding to similar changes of stressed state on this portion of the rod.

For a stress-strain state of the rod (isolines σ and *s*) at the final stage of the process (*t* = 51 min) (Fig. 4) it is characteristic that in the region of a die from the lateral mark 2 to 10 the stresses are negative and vary from –436 to –75 MPa. It corresponds to compression stress decrease with distance from a container. Further downward from mark 10 to 14 there is a wide zone of very low compression stresses about –3 MPa. On a free portion of the rod (outside the die) a vertical boundary goes between a very low negative compression stress in the centre –3 MPa and positive tensile stress 69 MPa. The largest stress value 4.7 is achieved close to and along the die wall up to some distance from the outlet hole. At a larger rod length, the stress varies moderately from 2.6 to 3.4. Only in the lowest part of the rod one can see stress drop to 0.4.

Thus, increase in the length of extruded rod produces a marked effect on the stress-strain state in the die region (compare Figs.3 and 4).

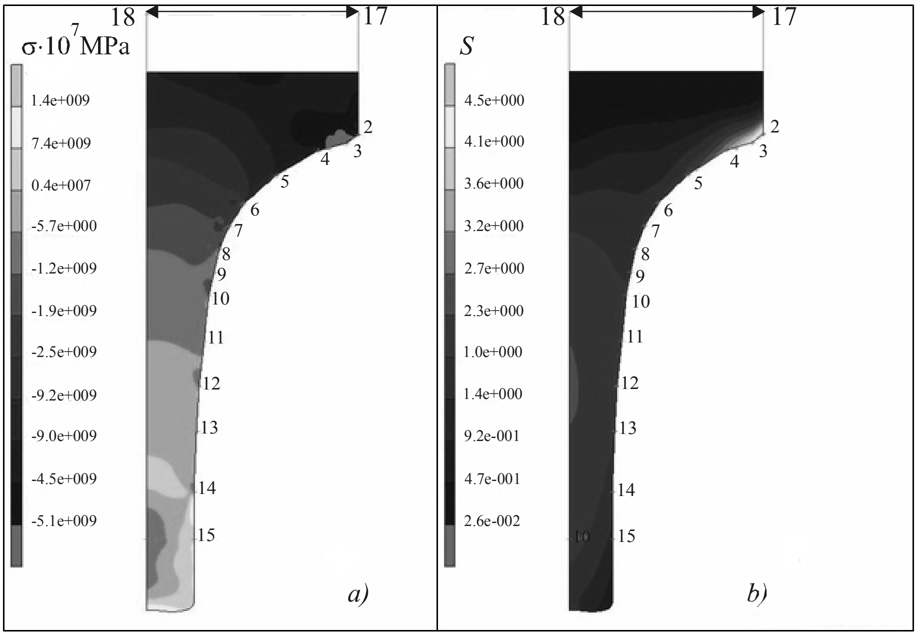

Fig. 3. Stress-strain state of sample leaving the die (t = 150 s):
a – isolines of the main maximum stresses σ; b – isolines of total maximum strains s.

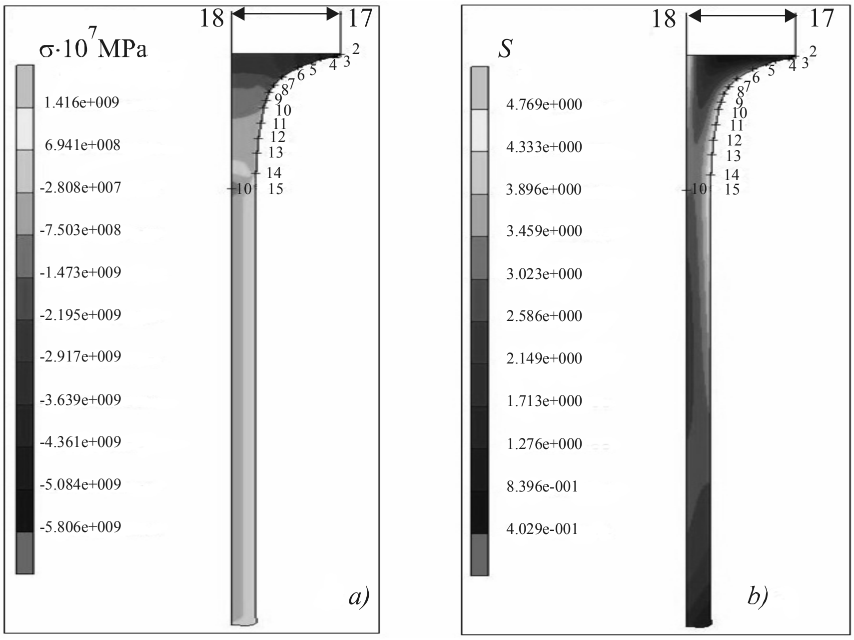

Fig. 4. Stress-strain state of the sample at the end of extrusion process (t = 51 min):
a – isolines of the main maximum stresses σ; b – isolines of total maximum strains s.

Results of structural studies

Metallographic and *X*-ray diffraction methods were used to study structural and textural changes along the length of an extruded rod of $Bi_{0.4}Sb_{1.6}Te_3$ solid solution.

To study the microstructure, the rod was cut along the extrusion axis. The texture was studied on plates cut from extruded rod perpendicular to extrusion axis. To estimate the texture, a method for construction of inverse pole figures based on diffractograms was used, i.e. the possibility of coincidence between poles of different planes and the extrusion axis was estimated. In the calculation of pole statistical weights, normalization by the rated values of reflection intensity was carried out.

Fig. 5 shows a microstructure of the initial part of an extruded rod cut along the extrusion axis.

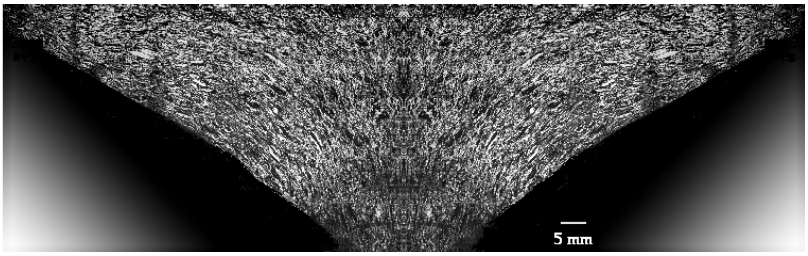

Fig. 5. Material microstructure in the initial part of the die.

In the initial billet, grains are elongated in the direction perpendicular to extrusion direction. In the transient region of the die there is grain reorientation with the result that they are aligned in a direction parallel to extrusion axis. In so doing, grain rotation is more intensive in the mid of the rod.

Fig. 6 shows a change in the texture and microstructure of the rod along the extrusion axis.

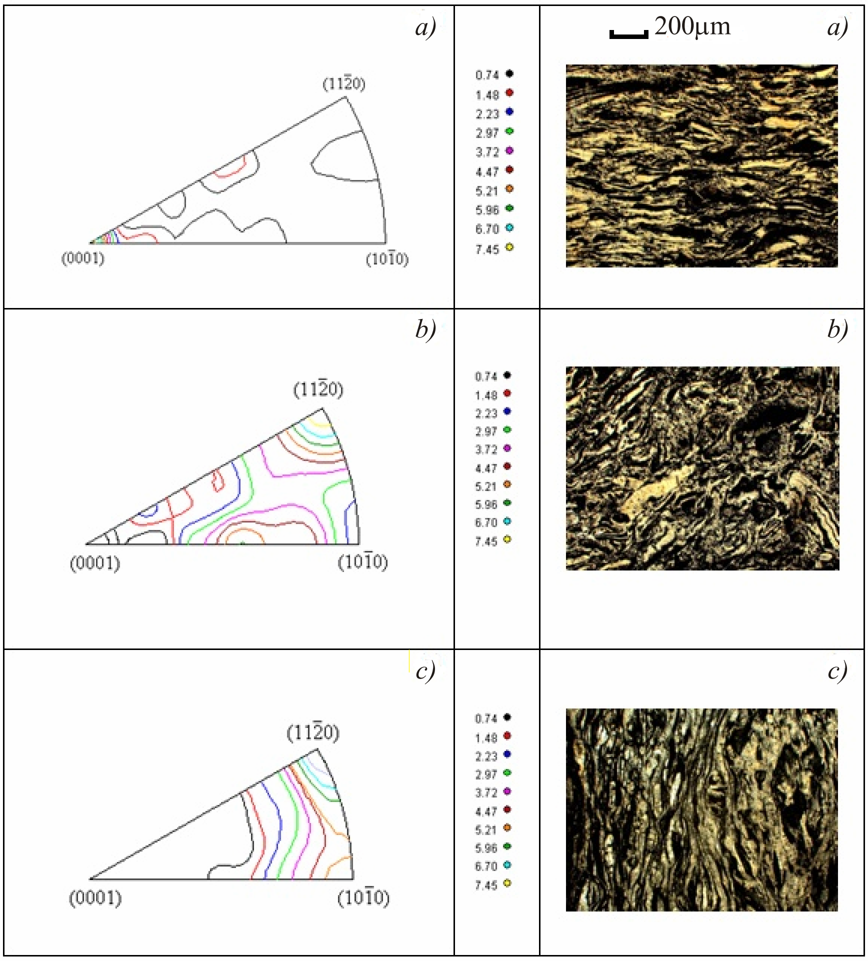

Fig. 6. A change in the texture and microstructure of the rod along the extrusion axis:
a – billet, b, c – at the distance of 2, 4 cm from the upper edge of the die.

At outlet from the die, deformation textures (11.0) and (10.0) are preferably formed, with their zone axis parallel to extrusion axis, whereby cleavage planes are also arranged along the extrusion axis. Then along the length of extruded rod the texture and microstructure remain basically unchanged. In so doing, there is a gradual disappearance of porosity present in the billet.

The fine structure of extruded rod was studied by scanning electron microscopy method. Unlike the fibrous structure of material in the die region, the grains in the extruded rod are equiaxial and have the size from 1 to 10 μm. As compared to the initial powder (hundreds of microns), the grain size in the extruded rod is smaller, the grain boundaries are sharply defined. A combination of these factors testifies to dynamic recrystallization in material. Dynamic recrystallization apparently occurs in the rod after the sample leaves the die where the temperature is rather high.

Conclusions

1. The basic zones of stress-strain state in the extruded rod in the region of the die affecting the formation of material structure are established.
2. Elongation of the extruded rod has a pronounced effect on the stress-strain state in the region of the die.
3. In the cylinder part of the die there is a radial inhomogeneity of stress that may lead to formation of longitudinal cracks under sufficiently high stress level.
4. Comparison of calculated results to structural studies has shown that the texture and microstructure of the extruded rod are formed in the region up to 4 cm from the upper edge of the die where stresses are highest possible.
5. Due to radial inhomogeneity of strain velocity in the region of the die, reorientation of elongated grains occurs faster in the mid of the rod.
6. After the extruded rod leaves the die, the texture and microstructure remain basically unchanged.

References

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