PECULIARITIES OF PRODUCTION N-$Bi_2(Te,Se)_3$ AND P-$(Bi,Sb)_2Te_3$ IN CONDITIONS OF STRUCTURAL SUPERPLASTICITY

O.B.Sokolov, S.Ya.Skipidarov, N.I.Duvankov, E.V.Zaitsev

Nord Co., Moscow, RUSSIA

INTRODUCTION

Superplasticity is important, primarily, due to the fact that intensive plastic deformations can be created under low loads, with the formation of material with a homogeneous structure in cross-section. The establishment of conditions providing for the apparent superplasticity acquires special importance for the realization of plastic deformation of thermoelectric materials [1]. For this purpose the authors have investigated the process of hot extrusion of N-$Bi_2(Te,Se)_3$ and P-$(Bi,Sb)_2Te_3$ metal-ceramic billets through conical matrix both in isobaric and isothermic conditions.

ISOBARIC CONDITIONS

In isobaric conditions the temperature dependences of strain rate have been investigated. Strain rate $\dot{\varepsilon}$ (its mean value) was calculated from the values of the degree strain ε and the time of the material residence in the strain concentration zone. In $\lg\dot{\varepsilon}$-1/T (Fig.1) coordinates, where T is the temperature of extrusion, experimental points lie on straight lines correlating with the Arrhenius's equation $\dot{\varepsilon} \sim \exp(-Q/RT)$, where Q is an apparent energy of activation of the plastic flow, R is the Rydberg constant.

Calculations show that in the zone of minimal rates the apparent energy of activation is maximal and amounts to 1.45 eV. With the medium rates the Q value dramatically decreases to 0.79 eV that indicates the changing of the strain mechanizm.

ISOTHERMIC CONDITIONS

In isothermic conditions the pressure dependences of the strain rate have been investigated. To the authors' opinion over 90% of pressure can be attributed to the

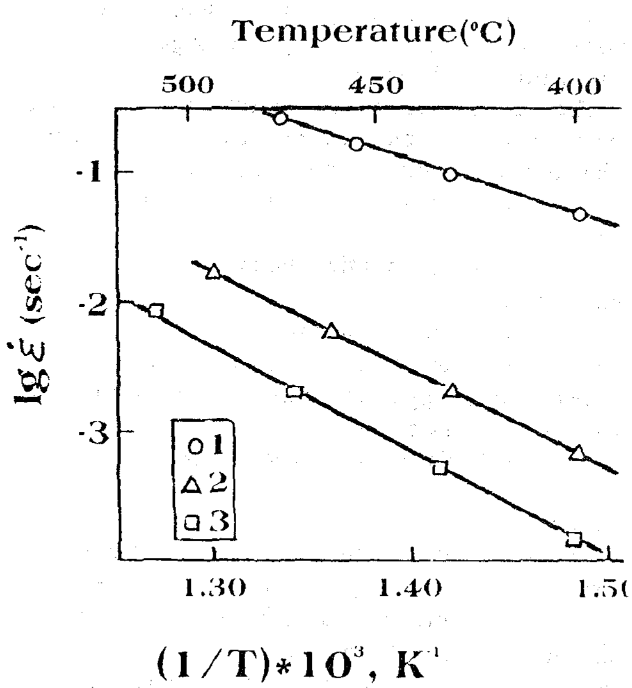

Fig.1. Temperature dependence of N-$Bi_2(Te,Se)_3$ plastic deformation rate under constant pressure of extrusion (kg/mm^2): 1- 50; 2- 80; 3- 100; stretching coefficient k=280.

resistance to the strain of material (S). Some straight-line zones of the obtained curves in logarithmic coordinates (Fig.2) are described by the equation $S = N \cdot \dot{\varepsilon}^m$, where N is a constant, *m* is a strain-rate sensitivity index. The changing incline of straight lines indicates that with the growth of the $\dot{\varepsilon}$ value the *m* value gradually decreases from ≈ 0.8 (for the N-type material) at rates ≤ 10^{-2} sec^{-1} to lower than 0.2 at maximal rates. It qaulitatively corresponds to the II and III stages of typical curves of superplasticity [2].

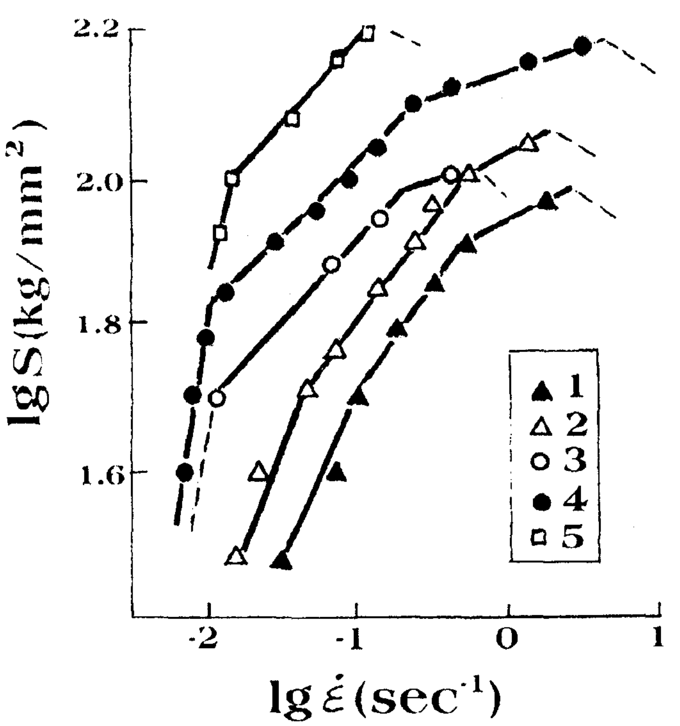

Fig.2. Pressure dependences of N-$Bi_2(Te,Se)_3$ (3, 4) and P-$(Bi,Sb)_2Te_3$ (1,2,5) plastic deformation rate at a constant temperature of extrusion: 480(1). 450(2); 440(3, 4). 400(5); k = 289 (1, 2, 4, 5); k=64 (3).

STRUCTURE

The results of the undertaken research into the structure by method of electronic microscopy (on splits) show that the particles of the original billet are characterized by a clearly demonstrated layer structure (Fig. 3a, 3d). At the initial stage of the process of plastic deformation the phenomenon of mechanical twinning is observed (Fig.3e). At the final stage of plastic deformation the structure is completely recrystallized in the P-$(Bi,Sb)_2Te_3$ material (Fig. 3b, 3c) and to a great extent in the N-$Bi_2(Te,Se)_3$ material (Fig.3f). The mean grain size amounts to approximately 2 - 3 mμ. It indicates, that superplasticity is realized through grain boundary sliding. Although grain boundary sliding (structural superplasticity) is predominant, a certain contribution of the diffusion creep and dislocation creep cannot be excluded. With high strain rates there is not enough time for the processes of recrystallization in the strain concentration zone, and the strain (extrusion) changes from superplasticity to conventional plasticity. In this case the samples demonstrate such a strain structure in which grains and intercrystallite impurities are stretched in the direction of extrusion.

DIFFUSION AND CHARACTERISTICS

To identify the nature of diffusion processes going in conditions of structural superplasticity the original cylinder-shaped billet has a thin interphase boundary. It was a plane stretching along the billet axis and dividing two tellurides which differed in metal composition (Fig.4). Research into diffusion by method of micro-X-ray spectrometry was effected on lateral and axial microsections which were perpendicular to the phase boundary.

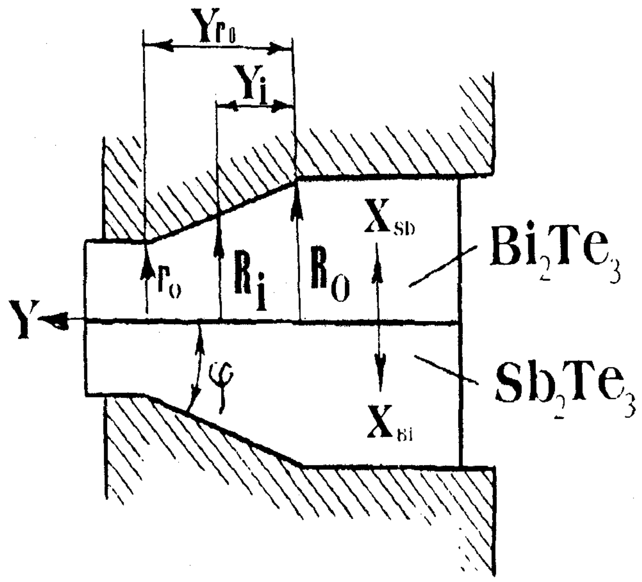

Fig.4. Design of a composite billet for the research into diffusion.

Concentration curves characterizing the distribution of Bi and Sb in pressing residue and extruded samples were taken by the MS-46 ("Cameca") X-ray installation. X-ray characteristical radiation of elements was registered for Sb on the $L_{\alpha 1}$ line and for Bi on the $M_{\alpha 1}$ line. The diameter of the electronic probe amounted to 1 mμ. By the above mentioned curves the depth of Sb penetration into Bi_2Te_3 and that of Bi penetration into Sb_2Te_3 was identified. Calculations were made with the use of Lyubov-Fastov's equation [3] for the diffusion in plastic deformation media

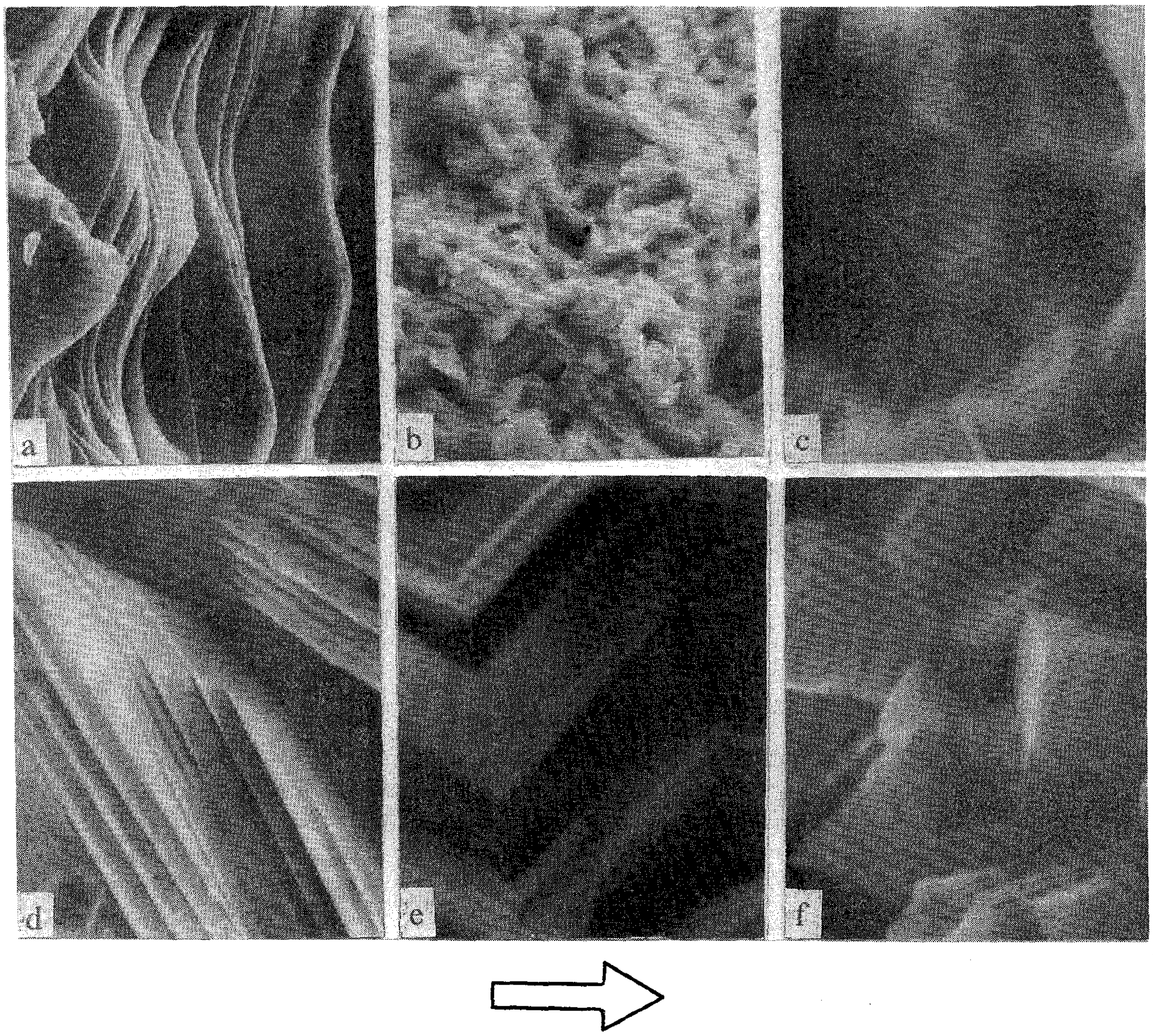

Fig.3. Changing of the microstructure with hot extrusion in conditions of structural superplasticity. P-$(Bi,Sb)_2Te_3$ structure: a - the original billet (10,000x); b - extruded rod (2 300x); c - extruded rod (10,000x). N-$Bi_2(Te,Se)_3$ structure: d- the original billet (10,000x); e - a mechanical twin on the boundary of the strain concentration zone (10,000x); f - extruded rod (10,000x). The arrow indicates the direction of extrusion.

with due account for the initial and boundary conditions which were determined by the geometry of extrusion tool (Fig.4). This equation is of the following form:

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \xi^2},$$

where

$$\xi = x \cdot \frac{R_0}{R(t)}, \quad \tau = \int_0^t R_0^2 / R(t)^2 \cdot D(t) \cdot dt.$$

Here, x is an experimentally observed depth of diffusion, ξ is the depth of diffusion with due account for the plastic deformation, τ is the time of diffusion in the period of plastic deformation; C is the concentration of the diffusant; D is the diffusion coefficient.

The equation was solved by the following way. Assuming that the square average value of the displacement of the diffusant is

$$\xi^2 = 2 C_1 \tau,$$

the differentiation result is: $\xi d\xi = C_1 R_o^2/R^2(t) \cdot D(t) \cdot dt$. The time of passing the y_i layer to the depth of $\Delta y_i = y_i - y_{i-1}$ amount to $\Delta t_i = t_i - t_{i-1}$ Having the time of passing through the Δy_i layer and y_{i-1} layer to the onset of the strain concentration zone one can identify on the basis of experimental data the time of the material residence in the Δy_i layer. The time of the process of deformation is the volume of pressing portion to flown-out material volume per second ratio:

$$t_i = \frac{R_i^3}{3 \cdot V \cdot tg\varphi \cdot r^2},$$

where V is the rate of material flow-out from the conical matrix;

$$\Delta t = \frac{(R_i - R_{i-1}) \cdot (R_i^2 + R_i \cdot R_{i-1} + R_{i-1}^2)}{3 \cdot tg\varphi \cdot r^2 \cdot V}.$$

Assuming that $R_i \approx R_{i-1}$ one can write the expression as follows:

$$\Delta t = \frac{\Delta R_i}{tg\varphi} \cdot \frac{R_i^2}{r^2 \cdot V}.$$

Assuming that $R_i/tg\varphi = y_i$, accordingly

$$\Delta R_i / tg\varphi = \Delta y_i,$$

this expression acquires the following form:

$$\Delta t = \Delta y_i \cdot \frac{R_i^2}{r^2 \cdot V} \approx dt.$$

Then

$$\xi \cdot d\xi = C_1 \cdot D_i \cdot 1/V_0 \cdot dy,$$

where V_0 is the rate of material feeding into the conical matrix. Whence the solution of the Lyubov-Fastov's equation derived with due account for the boundary and original conditions has the following form:

$$D_i = C_1 \cdot V_0 \cdot \xi_i \cdot \frac{\Delta \xi_i}{\Delta y_i},$$

where D_i is a diffusion coefficient of the chemical element in the Δy_i thickness layer of the system under consideration which is located in the conical strain concentration zone at the y_i distance from its onset; C_1 is a constant; $\xi_i = x_i R_o/R_i$ (x_i is the experimentally identified displacement of the diffusant; $2R_i$ is the diameter of the strained billet; $\Delta\xi_i = \xi_i - \xi_{i-1}$; V_o is the rate of the material feeding into the strain zone.

In experiment, on a microsection of the pressing residue in a matrix with a $\varphi = 30^\circ$ entry angle it was discovered that for the investigated elements (Bi and Sb) the $\xi_i(y_i)$ dependence is approximated by a straight line (Fig.5) with an accuracy of ±10%, i.e. $\xi_i = C_2 y_i$ and, accordingly, $\Delta\xi_i = C_2 \Delta y_i$. Then $D_i = CV_o y_i$, where $C = C_1 C_2$.

In the outset of the strain concentration zone ($y_i \geq y_{ro}$), i.e. in the extruded rod, $D_{ro} = CV_o y_{ro}$. It follows, that in the extruded rod the ε strain rate dependence of ξ_{ro} cannot occur that may be attributed to the proportional growth of the diffusion coefficient. The established proportional growth of the diffusion coefficient with the increase of the strain rate in the process of extrusion accounts for the stability of thermoelectric characteristics of extruded rods of N-$Bi_2(Te,Se)_3$ and P-$(Bi,Sb)_2Te_3$ solid solutions within a wide range of $\dot{\varepsilon}$ in conditions of structural superplasticity (Fig.6).

The practical aspect of the undertaken research is the opportunity to spur the processes of diffusion alignment of statistical microinhomogeneities [4] in the process of hot extrusion in conditions of structural superplasticity

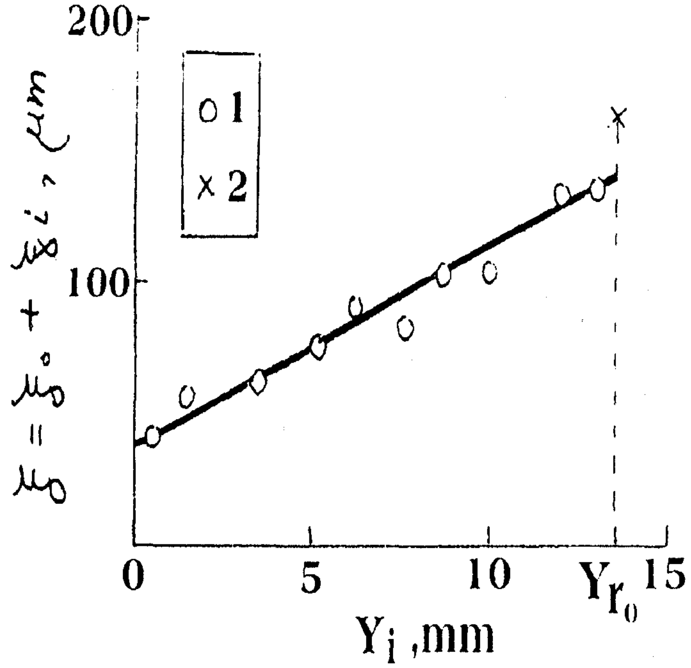

Fig.5. y_i dependence of Bi penetration into Sb_2Te_3: 1 - by the results of the analysis of the pressing residue (k = 44.5; φ = 30°) after extrusion with T = 480° C and V = 0.5 mm/sec.; 2 - data from extruded samples.

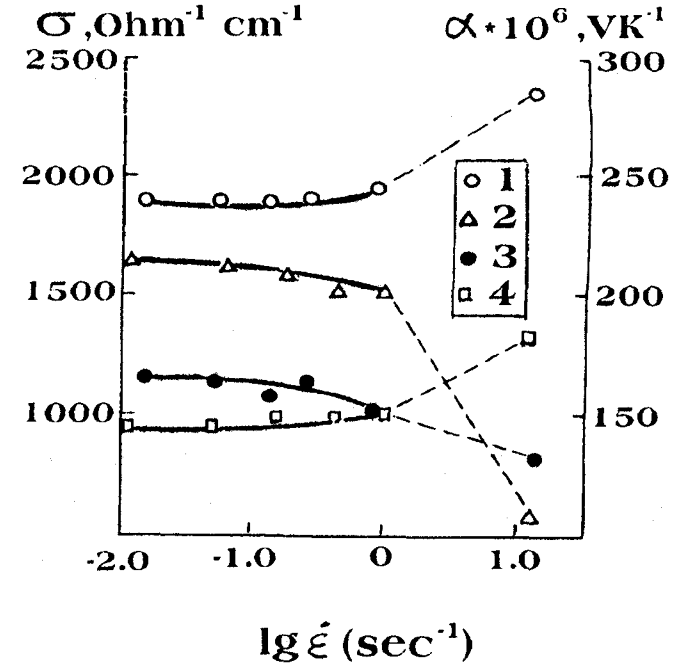

Fig.6. Strain rate dependence of electrical conductivity (1,2) and Seebeck coefficient (3,4) of P-$(Bi,Sb)_2Te_3$ (1,3) and N-$Bi_2(Te,Se)_3$ (2,4) samples extruded at k = 64.

through the reduction of the angle (φ) of entry into matrix (see Fig.4). It allows to produce the rods of over 20 mm diameter from N-$Bi_2(Te,Se)_3$ and P-$(Bi,Sb)_2Te_3$ metal-ceramic billets by method of extrusion.

CONCLUSIONS

In isobaric conditions, in the zone of minimal rates of plastic deformation the apparent energy of activation of plastic deformation of the N-$Bi_2(Te,Se)_3$ material is maximal and amounts to 1.45 eV. With medium rates the value of the energy of activation dramatically decreases to 0.79 eV that proves the changing of the strain mechanizm.

For isothermic conditions it was discovered, that with the increase of the strain rate the strain-rate sensitivity index for the N-$Bi_2(Te,Se)_3$ material decreases from the value of ~ 0.8 to that of lower than 0.2 which is attained at maximal rates. It qualitatively corresponds to the II and III stages of typical curves of superplasticity.

The results of the research into the structure by method of electronic microscopy show that the grain boundary sliding is the main micromechanizm of superplasticity of low-temperature thermoelectric materials.

The proportional growth of the diffusion coefficient with the increase of strain rate has been established. It accounts for the absence of strain rate dependence of thermoelectric characteristics of N-$Bi_2(Te,Se)_3$ and P-$(Bi,Sb)_2Te_3$ TE legs if the latter are produced in conditions of structural superplasticity.

REFERENCES

1. O.B. Sokolov, B.A. Efimova. On Resistance to Cracks of Semiconductive Materials, P-PbTe Case Study. Izvestiya AN SSSR. Neorganicheskiye Materialy (Non-organic Materials.). 1992. V.28, No 1. p.61 (in Russian).
2. O.A. Kaibyshev. Plasticity and Superplasticity of Metals, M., Mettalurgiya (Metallurgy), 1975. (In Russian).
3. B.Ya. Lyubov, N.S. Fastov. Physics of Metals and Physical Metallurgy, v.10, 2, 310 (1960), (in Russian).
4. A.I. Anukhin, S.Ya. Skipidarov, O.B. Sokolov. Statistical Micro-Inhomoheneities in $(Bi,Sb)_2Te_3$ Solid Solutions Grown from Melt with Excess Content of Tellurium, Proceedings of the 14th International Conference on Thermoelectric Energy Conversion, St.Petersburg, Russia, 1995, p.65.