Thermodynamics of Fragmentation of Solids at Severe Plastic Deformation

A.V. Khomenko[1,2,*], D.S. Troshchenko[1], D.V. Boyko[1], M.V. Zaharov[1]

[1] *Sumy State University, 2, Rymskii Korsakov Str., 40007 Sumy, Ukraine*
[2] *Peter Grünberg Institute-1, Forschungszentrum-Jülich, D-52425 Jülich, Germany*

Using the Landau theory of phase transitions the fragmentation of solids during the process of severe plastic deformation (SPD) is studied. In describing of appearing defect structures the density of grain boundaries, dislocations and entropy are introduced. This allows us to take into account the two channels of energy dissipation (thermal one and defects formation). In the deterministic case phase diagram is determined establishing the domains of realization of different types of structures. The interaction effect of several types of defects is investigated on the formation of limiting structure in terms of internal energy. As shown, the grains size in limiting structures decreases with an increase of the elastic strain. Within the scope of the adiabatic approximation, at which change of the dislocations density follows the evolution of the density of the grain boundaries, the conditions of formation for two limiting structures are found. They correspond to the mode, in which there is a mixture of grains of different sizes.

Keywords: Grain boundary, Dislocation, Phase transition, Limiting structure, Internal energy.

PACS numbers: 05.70. – a, 61.72.Mm, 62.20.F –, 64.10. + h, 64.60.My, 68.35.Md, 83.10. – y

1. INTRODUCTION

Processing of metals by methods of severe plastic deformation (SPD) is one of the most perspective methods for obtaining materials with the improved physical and mechanical properties [1]. But at the same time, it is the multi-level process a theoretical description of which is quite complex task. The problem consists of choosing the main parameters and reasonably neglecting the infinitude of others ones.

At present for describing the destruction of quasi-brittle materials [2,3], grain grinding during the process of their processing by methods of severe plastic deformation [4-6], behavior of a thin layer of lubricant [7-9] methods close to concept of Landau theory of phase transitions are developed. The evolution equations for the non-equilibrium variables can be derived by differentiating the multidimensional thermodynamic potential [10]. However, the existing theory is based on generalization of the experimental data and can't explain the reason for the formation of a limiting state [1], when for the next following cycle of SPD the grains cease fragmentation [11]. Also the connection between generation of several types of defects has not set, for example, such defects as grain boundary and dislocation. Their interaction can provide the formation of stationary domains in the phase diagram.

2. BASIC EQUATIONS

The conservation law of energy must be performed for both the external interactions of the selected volume and the internal transformations of several types of energy as a result of the flow of irreversible internal processes. Combining the first law of thermodynamics and the law of energy transformation on the internal degrees of freedom it is possible to obtain thermodynamic "identity" for density of internal energy u as

$$\mathrm{d}u = \sigma_{ij}\mathrm{d}\varepsilon_{ij}^e + T\mathrm{d}s + \sum_{l=1}^{N}T_l\delta s_l + \sum_{l=1}^{N}\varphi_l\delta h_l \ , \qquad (1)$$

where σ_{ij}, ε_{ij}^e are tensor of stress and elastic part of strain tensor; T, s , T_l, s_l are temperature and entropy of equilibrium and l-th nonequilibrium subsystem; φ_l and h_l are conjugate pair of thermodynamic variables, which shows the imperfection of a material (energy and defect density the type of l).

The nonequilibrium state is defined by set of parameters. The first two ε_{ij}^e and s describe part of the system which has already come to an equilibrium distribution (reversible processes), and other two s_l, h_l parameters represent nonequilibrium part (irreversible processes) [12].

The relationship (1) is written down in general form. The specific model of kinetics of structural defects will be determined, if we will define the dependence of the internal energy or effective internal energy on all independent variables of a problem [13,10]. Since the exact analytical solution has not known, so let's consider a simplified model. We will expand the effective internal energy into power series of its arguments. In this paper the two-level two-mode model is considered with the contribution of grain boundaries taking into account to the fourth degree relatively to their density [10].

The amount of modes is determined by the number of stable stationary solutions or maximums of internal energy. The number of levels is defined by the quantity of types of the considered defects. The grain boundary is the main structural defect during the process of SPD, but at the same time, dislocations take an important role in generation of power conditions for formation of grain boundaries.

The internal energy is represented by the relation:

---

* khom@mss.sumdu.edu.ua

01PCSI16-1

$$u\left(h_g, h_D\right) = u_0 + \sum_{m=g,D}\left(\varphi_{0m}h_m - \frac{1}{2}\varphi_{1m}h_m^2\right.$$
$$\left. +\frac{1}{3}\varphi_{2m}h_m^3 - \frac{1}{4}\varphi_{3m}h_m^4\right) + \varphi_{gD}h_g h_D \,, \qquad (2)$$

where u_0, φ_{km}, φ_{gD} are some coefficients which depend on the equilibrium variables s and ε_{ij}^e as control parameters:

$$u_0 = \frac{1}{2}\lambda(\varepsilon_{ii}^e)^2 + \mu(\varepsilon_{ij}^e)^2 + \beta s^2 \,, \qquad (3)$$

$$\varphi_{0m} = \varphi_{0m}^* + g_m\varepsilon_{ii}^e + \left(\frac{1}{2}\bar{\lambda}_m(\varepsilon_{ii}^e)^2 + \bar{\mu}_m(\varepsilon_{ij}^e)^2\right)$$
$$+\beta_m s + \beta_{gm}s\varepsilon_{ij}^e \,, \qquad (4)$$

$$\varphi_{1m} = \varphi_{1m}^* - 2e_m\varepsilon_{ii}^e \,, \qquad (5)$$

where λ, μ are elastic constants of the defect-free material; g_m is the variable which characterizes the activation of formation the corresponding defect; $\bar{\lambda}_m$, $\bar{\mu}_m$ are elastic constants, which caused by the existence of defects; e_m is the defect annihilation, which is activated by acting stress; ε_{ii}^e, $(\varepsilon_{ij}^e)^2 = \varepsilon_{ij}^e\varepsilon_{ji}^e$ are first and second invariants of strain tensor. Repeated indexes mean summation. Since compression process of the deformed object is described, so for the further analysis the negative values of the first invariant of strain tensor ε_{ii}^e are used.

The components of strain ε_{ij}^e are the control parameters, which represent the external influence, and they can be regarded as constants. In Eq. (2) the index of D belongs to dislocations, and the index of g to the grains boundaries.

A polynomial of fourth degree with positive coefficients φ_{km} in Eq. (2) can have two maximums (two modes). We will consider only simplified case of homogeneous distribution of dislocations, therefore the highest powers are neglected at the description of evolution of dislocations φ_{2D} and φ_{3D} [10].

For calculations the following set of parameters was accepted:

$$\varphi_{0D}^* = 5\cdot10^{-4}\,\text{J}\cdot\text{m}^{-1}, \varphi_{1D}^* = 0.6\,\text{J}\cdot\text{m}, \varphi_{1g}^* = 3.3\,\text{J}\cdot\text{m}^{-1},$$
$$g_D = 0.31\,\text{J}\cdot\text{m}^{-1}, \bar{\mu}_D = 1.05\,\text{J}\cdot\text{m}^{-1}, \bar{\lambda}_D = 0.96\,\text{J}\cdot\text{m}^{-1},$$
$$\bar{\mu}_g = 10.5\,\text{J}\cdot\text{m}^{-2}, \bar{\lambda}_g = 9.6\,\text{J}\cdot\text{m}^{-2},\ e_g = 1.55\,\text{J}\cdot\text{m}^{-1},$$
$$e_D = 0.155\,\text{J}\cdot\text{m},\ \varphi_{gD} = 0.03\,\text{J},\ \varphi_{0g}^* = 5\cdot10^{-3}\,\text{J}\cdot\text{m}^{-2},$$
$$\varphi_{2g} = 6.5\,\text{J}, \varphi_{3g} = 2.88\,\text{J}\cdot\text{m}, g_g = 9.1\,\text{J}\cdot\text{m}^{-2}.$$

The parameters that aren't listed are supposed to be equal to zero.

3. PHASE DIAGRAM

Let's write down the equation of evolution:

$$\tau_{h_l}\frac{\partial h_l}{\partial t} = +\frac{\partial\bar{u}}{\partial h_l} \,, \qquad (6)$$

where τ_{h_l} is the times of relaxation; h_l is the density of defects of l-type; $\bar{u}$ is the effective internal energy [10]. The system of evolution equations is defined in explicit form:

$$\tau_{h_D}\frac{\partial h_D}{\partial t} = \varphi_{0D} - \varphi_{1D}h_D + \varphi_{gD}h_g \,, \qquad (7)$$

$$\tau_{h_g}\frac{\partial h_g}{\partial t} = \varphi_{0g} - \varphi_{1g}h_g + \varphi_{2g}h_g^2 - \varphi_{3g}h_g^3 + \varphi_{gD}h_D \,. \qquad (8)$$

Let's use the adiabatic approximation $\tau_{h_g}\gg\tau_{h_D}$, at which the evolution of dislocations density follows the change of density of grains boundaries. In this case, we set $\tau_{h_D}\left(\partial h_D/\partial t\right)\approx 0$ in Eq. (7) and express h_D from this equation:

$$h_D = \frac{\varphi_{gD}}{\varphi_{1D}}h_g + \frac{\varphi_{0D}}{\varphi_{1D}}. \qquad (9)$$

Substituting the dependence of the dislocations density (9) into Eq. (8), the Landau-Khalatnikov equation is obtained:

$$\tau_{h_g}\frac{\partial h_g}{\partial t} = \frac{\partial V}{\partial h_g} \,, \qquad (10)$$

where derivative of the effective thermodynamic potential with respect to the density of grains boundaries $\partial V/\partial h_g \equiv F(h_g)$ specifies the thermodynamic force F:

$$F\left(h_g\right) = \varphi_{0g} + \varphi_{gD}\frac{\varphi_{0D}}{\varphi_{1D}} - \left(\varphi_{1g} - \frac{\varphi_{gD}^2}{\varphi_{1D}}\right)h_g$$
$$+\varphi_{2g}h_g^2 - \varphi_{3g}h_g^3, \qquad (11)$$

that tends to bring the parameter h_g to the attractor corresponding to steady-state value. The system is described by thermodynamic potential:

$$V\left(h_g\right) = \int_0^{h_g}F\left(h_g'\right)\mathrm{d}h_g'. \qquad (12)$$

This relationship is identical for a given type of defect to Eq. (2) at using the substitution (9).

Steady-state density of grains boundaries h_g is fixed by the extremum condition of potential (12), since at $\partial V/\partial h_g = 0$ according to Eq. (10) $\partial h_g/\partial t = 0$. Besides, the minimums of potential correspond to unstable states, but its maximums meet the stable states [13].

Stationary condition leads to the expression:

$$\varphi_{3g}h_g^3 - \varphi_{2g}h_g^2 + \left(\varphi_{1g} - \frac{\varphi_{gD}^2}{\varphi_{1D}}\right)h_g - \varphi_{0g} - \varphi_{gD}\frac{\varphi_{0D}}{\varphi_{1D}} = 0. \ (13)$$

Hence, the positions of extremums of potential depend on the parameters φ_{0g}, φ_{1g}, φ_{2g}, φ_{3g}, φ_{gD}, φ_{0D}, φ_{1D} and don't depend on the reference level of energy u_0. These extremums define the regimes of fragmentation during the SPD process.

The solution of equation (13) is shown in Fig. 1, according to which at small absolute values of invariant ε_{ii}^e three steady-states exist. Two of them correspond to the maximums of potential $V(h_g)$ (solid and dashed lines) and one to the minimum of potential (dotted line). The first maximum can be achieved at zero and non-zero values of the density of the grains boundaries h_{g0} depending on the value $(\varepsilon_{ij}^e)^2$. It takes non-zero values only in the case, when the value of strain $(\varepsilon_{ij}^e)^2$ is lager than certain critical value. This is due to the fact that during SPD the process of fragmentation can occur, when the elastic strain ε_{ij}^e and related with its stresses σ_{ij} exceed yield stress. Steady–states in the SPD process can be reached only after fulfillment of this condition. If it fails, the system can also approach the stationary states but with other and lower rate.
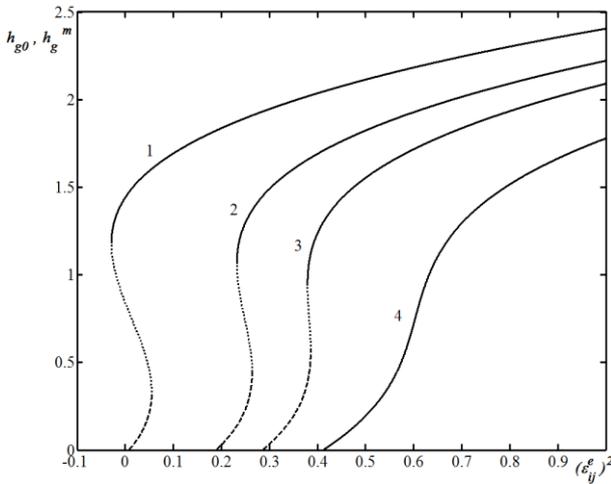

Fig. 1 − Dependence of the stationary values of the density of grains boundaries h_{go}, h_g^m on the second invariant of strain tensor $(\varepsilon_{ij}^e)^2$. The curves 1−4 correspond to the values $\varepsilon_{ii}^e = -0.01, -0.25, -0.42, -0.85$

According to the curves 1-3 the smaller of steady-states h_{g0} corresponds to the large size of grain (dashed parts of curves), the bigger of steady-states (solid sections of curves) meet the smaller grain size. They are separated by unstable state (dotted line) for the values of the density of grains boundaries which correspond to the minimum of potential. It is noteworthy that zero maximum meets the coarse-grained polycrystal and a single crystal in the limit. In the case of single crystal at first zero maximum of potential is realized and only when it becomes non-zero the process of fragmentation starts proceeding.

The sample is a single crystal (or coarse-grained polycrystal) for all curves shown in Fig. 1 for a value $(\varepsilon_{ij}^e)^2 = 0$. If we increase the value of strain $(\varepsilon_{ij}^e)^2$, then a single crystal ($h_{g0} = 0$) is realized for a while. According to the curve 1 with an increase of $(\varepsilon_{ij}^e)^2$ under the value, when zero and non-zero maximums of potential coexist, the process of fragmentation cannot realize, because these maximums are separated by potential barrier (dotted line). Then zero maximum becomes non-

zero (dashed line) and continuous process of fragmentation occurs. At further increase of strain the first maximum disappears coupled with potential barrier and the system by the first-order phase transition rapidly passes into the state, which is described by the second maximum of the potential (solid line). At the same time abrupt decrease of grains sizes takes place. It is known, that at the first-order phase transition the system can be in two metastable phases because of simultaneous presence of two maximums of thermodynamic potential [14]. Here this implies the coexistence of limiting structures with different grains sizes.

In the case that is described by the curves 2 and 3 as opposed to curve 1, realization of potential is impossible, which has at once zero and non-zero maximums. In other respects the curves 1-3 are the same.

If we continue to increase ε_{ii}^e for absolute magnitude (curve 4), the continuous second-order transition is realized from single crystal to fragmented sample in the absence of potential barrier. Besides, the formation of only one limiting structure is possible.

The critical value of second invariant of strain tensor is obtained from Eq. (13) for $h_{g0} = 0$:

$$\left(\varepsilon_{ij}^e\right)_c^2 = -\frac{1}{\left(\varphi_{1D}\bar{\mu}_g + \varphi_{gD}\bar{\mu}_D\right)}\left(\left(\frac{1}{2}\bar{\lambda}_g\varphi_{1D} + \frac{1}{2}\bar{\lambda}_D\varphi_{gD}\right)\left(\varepsilon_{ii}^e\right)^2\right.$$
$$\left. + \left(g_g\varphi_{1D} + g_D\varphi_{gD}\right)\varepsilon_{ii}^e + \left(\varphi_{0g}^*\varphi_{1D} + \varphi_{0D}^*\varphi_{gD}\right)\right). \quad (14)$$

In the coordinates $(\varepsilon_{ij}^e)^2 - \varepsilon_{ii}^e$ Eq. (14) represents the second-order curve below which the steady-state solution of Eq. (13) exists corresponding to the maximum of $V(h_g)$ at the point of $h_{g0} = 0$.
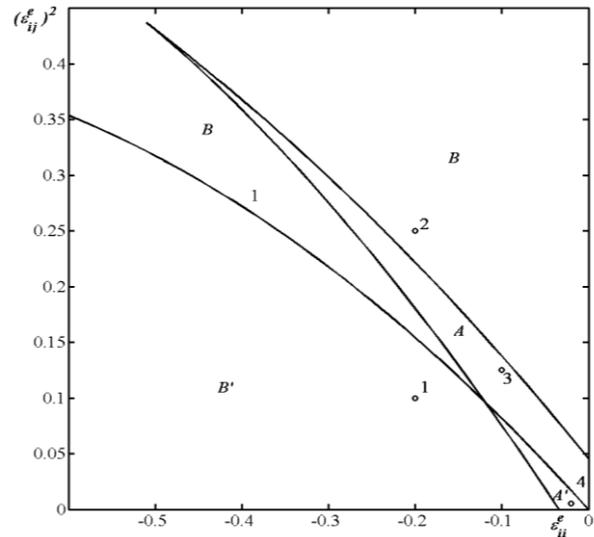

Fig. 2 − Phase diagram of the system with realization of domains of two (A, A') and one (B, B') limiting structures

The phase diagram is depicted in Fig. 2. The lines correspond to loss of system stability. The curve 1 is defined by the expression (14), below which zero steady-state solution is possible. There isn't channel of energy dissipation for the value $h_{g0} = 0$, which is related with the formation of defect structure, and system is

a single crystal or close to it structure. The points 1-4 in the phase diagram correspond to potential curves in Fig. 3, which possess the maximums. Their positions are defined by the parameters of the problem.
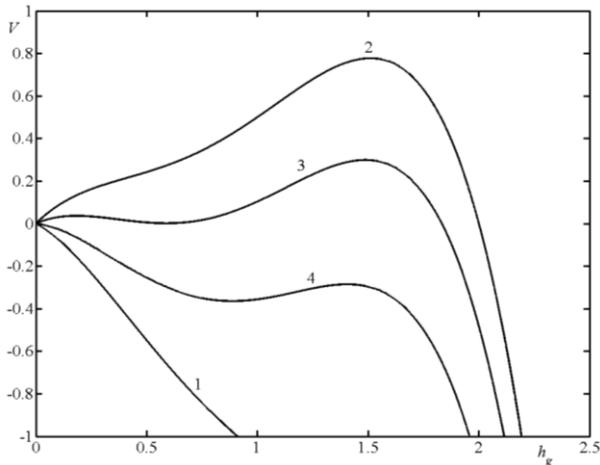

Fig. 3 − Dependence of the thermodynamic potential $V(h_g)$ (12) on the density of grains boundaries h_g. The curves $1-4$ correspond to the values of second invariant $(\varepsilon_{ij}^e)^2 = 0.1, 0.25, 0.125, 0.005$ and accordingly, the first invariant $\varepsilon_{ii}^e = -0.2, -0.2, -0.1, -0.02$ (points $1-4$ in Fig. 2)

The domain A corresponds to the realization of two non-zero maximums of potential $V(h_g)$ (curve 3 in Fig. 3). Here two limiting structures are observed with large (first maximum of potential) and small (second maximum of potential) size of the grains.

The region A' of the diagram is similar to domain A, but with the main difference that first maximum of the potential is zero (curve 4 in Fig. 3). Since the first limiting structure is formed for the value $h_{g0} = 0$, so it is a single crystal. In this region as a result of SPD process the fragmentation of material may not be realized. It is worth noting that the transitions between maximums of potential are possible directly during SPD process. Owing to them in regions A, A' two limiting structures are formed, which correspond to regime, that has the grains with different sizes. When SPD process is finished, it should be supposed that the sample has formed and the further transitions are not realized.

In domain of large strain B according to the curve 2 in Fig. 3 one limiting structure is generated. It is shown that with increase in elastic strain $(\varepsilon_{ij}^e)^2$ the grain size decreases and in the limit $(\varepsilon_{ij}^e)^2 \to \infty$ the sample represents amorphous structure.

The only one zero maximum of $V(h_g)$ (curve 1 in Fig. 3) is realized in the domain of small strains B'. Here the system is a single crystal.

4. CONCLUSIONS

Study based on the principles of the Landau theory of phase transitions is presented. The two-level two-mode model of non-equilibrium evolution thermodynamics in expressions of internal energy was assumed as a basis. In the capacity of main structural defect the grain boundary and dislocation are chosen.

This approach allows us to describe existence of limiting grain structure (non-zero maximum of thermodynamics potential) which is achieved as a result of SPD process. The coarse-grained state of material (in a limit single crystal) meets the zero maximum of energy and it is examined as a limiting structure which is equilibrium relatively to the ordinary plasticity in the context of theory. It is shown that transition from a coarse-grained structure to fine-grained one during SPD process can take place according to the scenarios of first- and second-order phase transitions. The phase diagram was build, where the values of first two invariants of elastic part of strain tensor ε_{ii}^e and $(\varepsilon_{ij}^e)^2$ define the domains of realization of various types of limiting structures.

REFERENCES

1. Ja. E. Beygelzimer, *Mech. of Materials* **37**, 753 (2005).
2. L.S. Metlov, A.F. Morozov, *Physics and Technics of High Pressures* **11** No2, 93 (2001).
3. L.S. Metlov, arXiv:0711.0399v1.
4. L.S. Metlov, *Phys. Rev. E* **81**, 051121 (2010).
5. L.S. Metlov, *Metallofiz. Nov. Tekh.* **29**, 335 (2007).
6. A.V. Khomenko, Ya.A. Lyashenko, L.S. Metlov, *Metallofiz. Nov. Tekh.* **30**, 859 (2008).
7. A.V. Khomenko, N.V. Prodanov, К.P. Khomenko, D.S. Troshchenko, *J. Nano- Electron. Phys.* **6**, 01012 (2014).
8. A.V. Khomenko, I.A. Lyashenko, *Tech. Phys.* **50**, 1408 (2005).
9. A.V. Khomenko, Ya.A. Lyashenko, *Tech. Phys.* **55**, 26 (2010).
10. L.S. Metlov, *Nonequilibrium evolution thermodynamics and its applications* (Donetsk: Noulidge: 2014).
11. Ya.E. Beygelzimer, V.N. Varyukhin, D.V. Orlov, S.G. Synkov, *Twist extrusion – process of deformation accumulation* (Donetsk: TEAN: 2003).
12. L.S. Metlov, arXiv:1312.3602v1.
13. L.S. Metlov, arXiv:1309.6791v1.
14. L.D. Landau, E.M. Lifshitz, *Course of theoretical physics, Vol.5: Statistical Physics* (London: Butterworth: 1999).