PHYSICAL REVIEW E **90**, 022124 (2014)

Nonequilibrium dynamics of a two-defect system under severe load

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(Received 19 February 2014; revised manuscript received 18 May 2014; published 21 August 2014)

In the framework of a two-defect model, based on a variation of the Landau technique, the kinetics of structural defect generation in solids under severe external load is investigated. The approach is based on a special form of kinetic equation in terms of internal energy, which is applied here to the description of an important practical problem of fine-grained structure formation in metals under severe plastic deformation. It unifies strengthening curves over the entire range of deformation, including the Hall-Petch and linear strengthening sections.

DOI: 10.1103/PhysRevE.90.022124 PACS number(s): 05.70.Ce, 05.70.Ln, 61.72.Bb

I. INTRODUCTION

An idea to introduce the internal state variable was proposed by Duhem in 1903 [1] and further developed in 1928 by Herzfeld and Rice, who defined the dispersion and attenuation of sound in polyatomic gases [2] (for details, see observations in Ref. [3]). This idea bore two different approaches: the internal state variable methods [4–6] (based on rational mechanics principles [7]) and the Landau approach [8–10]. There is no impenetrable boundary between these approaches since both are based on the same fundamental idea. The main difference is that the internal state variable approach starts with the principles and postulates of continuum or ordinary thermodynamics [11], while the Landau approach is based on a combination of variational and energetic (thermodynamic) principles. There is a clear interest in comparing the two approaches [12].

In modern science the applications of the Landau approach may in turn be subdivided into two large groups. The phase field method is one of the most adequate primary postulates of the Landau theory and although it does not have a strict statistical ground, the models based on this method describe real objects surprisingly realistically. This direction is presently under active development [13–17]. This makes it necessary to reevaluate the initial principles and postulates of the original Landau theory.

The second group of works is based on strict statistical principles taking into account fluctuation effects using modern notions, methods, and expedients such as methods of statistical physics and renormalization-group theory [18–21]. It is applied to phenomena requiring precise account of fluctuations, such as the critical phenomena and phase transitions.

All nonequilibrium processes occurring in a thermodynamic system can be divided into spatially homogeneous and heterogeneous ones. Homogenous processes are a kind of abstraction, but their description is simpler and it can be realized in the framework of a set of ordinary differential equations [11,22–24] or in the framework of the Landau-Khalatnikov evolution equations [9]. These frameworks are generally applicable for the description of small systems or systems with mixing [25]. The description of heterogeneous processes can be achieved in the framework of the continuum (gradient) approach or in the framework of the Ginzburg-Landau evolution equation[10], which is also nonlocal.

The development of mesoscopic nonequilibrium thermodynamics of soft matter with mesoscopic structural elements followed [26,27]. It is based on considering the entropy production, which is an important quantity at the mesoscopic level of condensed-matter organization; it also describes kinetic and thermodynamic properties of entropic barrier dynamics well.

To study the problem of metal treatment by severe plastic deformation (SPD) methods [28,29] another approach, which is a variation of the Landau technique, was proposed [3,30–32]. The approach combines the elements of classic nonequilibrium thermodynamics (generalization of the Gibbs relation) and the Landau theory of evolution equations. To achieve such a combination the evolution equations are formulated in terms of the internal energy (instead of the free energy). In addition, defect densities (of vacancies, dislocations, grain boundaries, etc.) are used as an order parameter or the configurational entropy.

An important problem of metal treatment by SPD requires a theoretical description of the laws of strengthening and dependences of yield stresses on the parameters of the system and, above all, on the average size of grains. It is known that when the grain size is large (of the order of a few micrometers) such a dependence obeys the Hall-Petch law [33–35]. A departure from the Hall-Petch law was found in the region of grain sizes around a few dozen nanometers [29,36–38], which manifests itself as a linear dependence of yield stresses on the reverse size grain [39,40].

The existing theoretical approaches are both too general and too complex [41–43] to yield a practical solution of the problem or, vice versa, they are too particular or specific [44–47] to reproduce the strengthening laws in a wide range of deformations. The proposed approach is general and at the same time is able to describe both the Hall-Petch law and the linear strengthening law from common grounds.

The present paper is devoted to the development of a variation of the Landau approach. In Sec. II some general issues of the approach are presented. In Sec. III the approach is applied to the description of defect kinetics during metal treatment by severe plastic deformation. Section IV contains a discussion. Section V summarizes our conclusions.

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II. SOME ISSUES OF THE APPROACH

A. Gibbs relations

The fundamental inequality of thermodynamics, combining its first and second laws, for solids in a general case can be written

$$dU \leqslant V\sigma_{ij}d\varepsilon_{ij} + TdS, \tag{1}$$

where U is the internal energy, V is the volume of the system, σ_{ij} and ε_{ij} are the stress and deformation tensors, and T and S are temperature and entropy. For plastic solids the deformation can be represented as a sum of reversible (elastic) ε_{ij}^{e} and irreversible (plastic) ε_{ij}^{n} contributions. In addition, the entropy increment can be represented as a sum of the entropy inflow from the external sources d_eS and from the irreversible internal processes d_iS [48,49], so the inequality (1) can be rewritten in the form

$$dU \leqslant V\sigma_{ij}d\varepsilon_{ij}^{e} + V\sigma_{ij}d\varepsilon_{ij}^{n} + Td_iS + Td_eS. \tag{2}$$

Here the first term represents the reversible portion of the work, which is stored in the form of elastic energy; the second term describes the irreversible part of the work, expended on the change of the internal structure of the solid and on its internal heating. The third term describes the increment of the heat due to the irreversible internal processes [48] and the last term is the influx of heat due to the external sources (thermostats).

If there is only one channel of energy dissipation in a solid (for example, plastic deformation during the stage of easy sliding of dislocations), which transforms the work directly into heat via the internal friction, then, due to the energy conservation, an equality and an inequality

$$V\sigma_{ij}d\varepsilon_{ij}^{n} = Td_iS \geqslant 0 \tag{3}$$

take place. Here the inequality $Td_iS \geqslant 0$ is the Clausius inequality in the usual form [48] and the inequality $\sigma_{ij}d\varepsilon_{ij}^{n} \geqslant 0$ is the same Clausius inequality, expressed via the irreversible work [50–53]. The equality $V\sigma_{ij}d\varepsilon_{ij}^{n} = Td_iS$ means that for one-channel model all the irreversible work is converted into heat [54]. The equality on the right-hand side of (3) takes place in the equilibrium case.

Thus, in the fundamental inequality (2) the same quantity of energy is included twice. If this replica is deleted, the fundamental inequality of thermodynamics can be presented as an equality in two equivalent forms

$$dU = V\sigma_{ij}d\varepsilon_{ij} + Td_eS, \tag{4}$$

$$dU = V\sigma_{ij}d\varepsilon_{ij}^{e} + TdS. \tag{5}$$

Both forms are valid for reversible and irreversible processes. The last form of the (Gibbs) equality is more convenient since it uses the reversible variable ε_{ij}^{e} and the total entropy S. In this form the internal energy is a single-valued function of its arguments $U = U(\varepsilon_{ij}^{e},S)$.

In the presence of two channels of energy dissipation (for example, during intensive generation of dislocations) the law of energy transformation is more complex

$$V\sigma_{ij}d\varepsilon_{ij}^{n} = Td_iS + \varphi dH \geqslant 0, \tag{6}$$

where φ and H are the energy and the number of defects. Here the second law of thermodynamics is obeyed when $d_iS \geqslant 0$. This is because the process of defect generation $dH_l \geqslant 0$ is always accompanied by conversion of part of the energy into heat [3], which makes the entropy increment positive $d_iS \geqslant 0$.

In the general case, when N_{def} types of defects are present, the Gibbs equality takes the form

$$dU = V\sigma_{ij}d\varepsilon_{ij}^{e} + TdS + \sum_{l=1}^{N_{\text{def}}}\varphi_l dH_l, \tag{7}$$

where φ_l and H_l are the energy and the number of defects of type l. By virtue of Eq. (7) the internal energy is a single-valued function of all its arguments $U = U(\varepsilon_{ij}^{e},S,H_l)$. The set of independent variables ε_{ij}^{e}, S, and H_l specifies an extended state of system. The variables ε_{ij}^{e} and S are equilibrial in nature; the variable H_l can be both equilibrial and nonequilibrial. In the latter case the system needs to be closed using the evolution equations.

Note that attempts to express the inequality (1) in the form of an equality were made before [55–58]. However, they were based on the introduction of additional variables, which characterize the internal processes formally without specification of their real nature. Here the variables are directly associated with the formation of specific structural defects in solids (metals).

B. Internal energy

The crucial difference in the proposed variant of the Landau technique, which sets it apart from the classical scheme, is usage of the internal energy as the main thermodynamic potential. Up to now, the main, if not the sole, stress was laid on the use of the free energy. At the same time, the internal energy is the most clearly determined physical quantity characterizing the system; it is basic not only for thermodynamics, but for all branches of physics. This energy directly enters the first law of thermodynamics; it is defined for both equilibrium and nonequilibrium states. In addition, it defines the generalized thermodynamic force within the framework of statistical consideration [32]

$$\varphi_l = \frac{\partial U}{\partial H_l}. \tag{8}$$

The variable φ_l corresponds to the average energy or chemical potential of defects. On the other hand, Eq. (8) is the definition of the generalized thermodynamic force. This definition, however, is not postulated here, but follows logically as part of the procedure for finding the equilibrium state. Consequently, the equilibrium value of φ_l must enter the evolution equation, which, with Eq. (8), can be written as

$$\frac{\partial H_l}{\partial t} = \gamma_l(\varphi_l - \varphi_{le}), \tag{9}$$

where γ_l is the kinetic coefficient, φ_{le} is the value of the defect energy in the equilibrium state, the difference $\varphi_l - \varphi_{le}$ is the thermodynamic force, and the time derivative on the left-hand side is the thermodynamic flux. Equation (9) describes the overdamped and deterministic dynamics of nonconserving and homogeneous parameters H_l.

A substantial difference when considering the problem in terms of the internal energy is that the generalized force (8) is not zero in the equilibrium state and, consequently, the extremal principle does not hold for the internal energy. This deficiency is compensated by the applicability of the generalized force definition (8) to both equilibrium and nonequilibrium states. If the equilibrium energy of the defect is known (not necessarily from statistical considerations), its value can be directly substituted into the kinetic equation (9).

The second postulate, which distinguishes this approach from the traditional one, is the use of the density of defects as an independent thermodynamic variable instead of the configurational entropy. Note that this variable is used not in parallel with the configurational entropy, but instead of it. A one-to-one correspondence between the density of defects and the configurational entropy may serve as a foundation for this principle. In the case of a solid with vacancies such a one-to-one correspondence follows from the fundamental Boltzmann relationship $S_c = k_B \ln W$ and from the definition of W (see, for example, [32]). For other types of defects this relation is unknown, but still can be expected to be unambiguous.

It should be noted that the influence of structural (topological) defects and direct participation of the defects of fluctuational nature in phase transitions were probed before [19,21]. However, here we examine the problem of simultaneous generation of two structural defect types (e.g., dislocations and grain boundaries) under severe external influence, while taking into account their mutual interaction throughout the process.

III. TWO-DEFECT MODEL OF SPD

Processes taking place during SPD are complex and affect all levels of structural defects: point defects (vacancies and interstitial atoms), linear defects (dislocations, disclinations, and triple joints), $2D$ defects (grain boundaries), and volume defects (micropores, microcracks, clusters). However, taking into account all types of defects significantly complicates the consideration. Let us therefore consider a simplified model, considering only those defects that play the most substantial role in fine-structure formation and significantly influence the material properties.

The most important defect type to consider must be the grain boundaries (GBs) since they directly determine the degree of fineness of a material. The next most important are the dislocations, which are responsible for the material strengthening. Other defects will not be directly taken into account here, although their presence is indirectly reflected by the values of phenomenological constants. Thus, in the process of SPD only these two types of defects play a crucial role, which predetermines the two-defect nature of the problem.

A. Evolution equations

Thus, by setting the dependence of the internal energy on its arguments, we fully define our problem in a thermodynamic context. Using Landau's idea, let us consider a homogeneous problem, taking the internal energy in the form of a polynomial dependence

$$u = u_0 + \sum_{l=g,D} \left(\varphi_{0l} h_l - \varphi_{1l} h_l^2 + \varphi_{2l} h_l^3 - \varphi_{3l} h_l^4\right) + \varphi_{gD} h_g h_D, \tag{10}$$

where u_0, φ_{kl} $(k = 0,1,2,3; l = g,D)$, and φ_{gD} are coefficients depending on the equilibrium variable ε_{ij}^e (as a control parameter)

$$\begin{aligned} \varphi_{0l} &= \varphi_{0l}^* + g_l \varepsilon_{ii}^e + \tfrac{1}{2} \bar{\lambda}_l \left(\varepsilon_{ii}^e\right)^2 + \bar{\mu}_l \left(\varepsilon_{ij}^e\right)^2, \\ \varphi_{1l} &= \varphi_{1l}^* - 2 e_l \varepsilon_{ii}^e, \end{aligned} \tag{11}$$

where φ_{0l}^*, φ_{1l}^*, g_l, $\bar{\lambda}_l$, $\bar{\mu}_l$, and e_l are phenomenological parameters of the model. The indices g and D are related to grain boundaries and dislocations, respectively. For the sake of convenience, the number of defects H_l was replaced by their volume densities h_l and similarly $S \to s$ and $U \to u$.

Let us consider the physical meaning and values of coefficients in the governing relations (10) and (11). The coefficient φ_{0g} corresponds to the total surface energy density of a regular (infinite) grain boundary. For a cold-roll treatment this energy may be taken to be equal to double the energy of a free surface of the same material [59–61]. For example, in copper it can reach the value of approximately 2×2 J/m^2. The first term φ_{0g}^* in this context is the self-energy of a boundary without the contribution from other factors. It is considered to be well relaxed, that is, at a minimum of its surface energy. This energy makes 15–20 % of the free-surface energy of the material [62]. That is, for copper it is approximately $0.2 \times 2 = 0.4$ J/m^2 (Table I).

In the case of compressive hydrostatic stress ($\varepsilon_{ii}^e < 0$) the contribution from the second term $g_g \varepsilon_{ii}^e$ decreases the GB energy. This is of great physical importance since the grain boundaries can be considered to be the sites of the density lack (or voids), distributed along a surface. These sites give the highest contribution to the energy of boundaries. When, due to external pressure, the volume of voids decreases, the boundary energy decreases too. At an elastic deformation of 0.2% for the copper, which corresponds to a tension ∼180 MPa, the constant g_g can be taken to be around 12 J/m^2 (see Table I).

TABLE I. Parameters of the two-defect model.

φ_{0g}^* (J m^{-2})	g_g (J m^{-2})	$\bar{\lambda}_g$ (J m^{-2})	$\bar{\mu}_g$ (J m^{-2})	φ_{1g}^* (J m^{-1})	e_g (J m^{-1})	φ_{2g} (J)	φ_{3g} (J m)
0.4	12	2.5×10^5	6×10^5	3×10^{-6}	3.6×10^{-4}	5.6×10^{-13}	3×10^{-20}
φ_{0D}^* (J m^{-1})	g_D (J m^{-1})	$\bar{\lambda}_D$ (J m^{-1})	$\bar{\mu}_D$ (J m^{-1})	φ_{1D}^* (J m)	e_D (J m)	φ_{2D} (J m^3)	φ_{3D} (J m^5)
5×10^{-9}	2×10^{-8}	0	3.3×10^{-4}	10^{-24}	6×10^{-23}		

For this value of g_g the energy of grain boundaries decreases to within 10% of its value for a relaxed boundary.

The contribution of terms proportional to $\bar{\lambda}_g$ and $\bar{\mu}_g$ in Eq. (11) at the same level of elastic stresses of 180 MPa must be such that the total effective energy of the GB does not exceed the double energy of the free surface (4 $\mathrm{J/m^2}$ for copper). This condition allows us to choose the constants $\bar{\lambda}_g = 0.25 \times 10^6\ \mathrm{J/m^2}$ and $\bar{\mu}_g = 0.6 \times 10^6\ \mathrm{J/m^2}$ (see Table I). The values of these constants are different because the effects of shear are of greater significance for the structural rearrangement of the solid.

The other constants are chosen from the requirement that the equilibrium (stationary) values of the GB density are inside the experimentally observed range. For grain boundaries this gives two steady states with a density around $h_g^{st1} = 10\ \mathrm{mm^{-1}}$ and $h_g^{st2} = 10\ \mu\mathrm{m}^{-1}$ with corresponding average grain sizes of 100 μm and 100 nm.

The same reasoning can be applied to dislocations. The minimum of dislocation energy in the absence of other factors for copper equals approximately $\varphi_{0D}^{*} = 5 \times 10^{-9}$ J/m [63] (see Table I).

The parameter responsible for the interaction between dislocations and grain boundaries is $\varphi_{gD} = 10^{-16}$ J. The time step in numerical calculations is $\tau = 0.67 \times 10^{-6}$ s and the kinetic coefficients are $\gamma_D = 5 \times 10^{23}$ J m s and $\gamma_g = 10^6\ \mathrm{J\,m^{-1}\,s}$.

Using Eq. (8), which is justified for both the equilibrium and nonequilibrium cases, and Eqs. (10) and (11), the evolution equation (9) can be represent in the form

$$\begin{aligned}\frac{\partial h_D}{\partial t} &= -\gamma_D[\varphi_{1D}(h_D - h_{De}) + \varphi_{gD}(h_g - h_{ge})],\\ \frac{\partial h_g}{\partial t} &= -\gamma_g[\varphi_{gD}(h_D - h_{De}) + \Phi(h_g - h_{ge})],\end{aligned} \qquad (12)$$

where

$$\Phi = \varphi_{1g} - \varphi_{2g}(h_g + h_{ge}) + \varphi_{3g}\left(h_g^2 + h_g h_{ge} + h_{ge}^2\right) \qquad (13)$$

and h_{De} and h_{ge} are the equilibrium values of h_D and h_g. It can be seen that the evolution equations do not depend explicitly on φ_{0D} and φ_{0g}, but may depend on them indirectly via the equilibrium values of h_D and h_g. This dependence can be extracted from the condition of the maximum of the probability distribution function of the system states. For the basic defects participating in SPD this function is unknown, which creates some difficulties in applying the theory to specific systems. To overcome them, let us now consider an effective potential approach in terms of the internal energy.

B. Effective potential approach in terms of the internal energy

Let us assume that the equilibrium energy of defect φ_{le} weakly depends on the current value of the defects density so that it can be brought under the sign of differentiation in Eq. (9). Then one can introduce an effective internal energy

$$\bar{u} = u - \sum_{l=1}^{N_{\mathrm{def}}} \varphi_{le} h_l. \qquad (14)$$

The evolution equation (9) takes the form

$$\frac{\partial h_l}{\partial t} = \pm\gamma_l \frac{\partial \bar{u}}{\partial h_l}. \qquad (15)$$

The plus sign here corresponds to the case when the equilibrium value of φ_{le} is in the region of convexity of the internal energy u, while the minus sign is for the concavity region [3]. In the first case a stationary solution corresponds to a maximum of the effective energy, in the second case to a minimum. Formally, Eq. (15) realizes an extremum principle since its stationary points coincide with maxima or minima of the effective potential of the internal energy $\bar{u}$. Equation (15) describes overdamped and deterministic dynamics for nonconserved and homogeneous order parameters (density of defects).

If the effective internal energy $\bar{u}$ is taken in the same form (10) as the initial internal energy u and with the same presentation coefficients (11) with the only difference that the equilibrium energy of φ_{le} is included as part of the coefficient of φ_{0l}, that is, $\varphi_{0l} \to \varphi_{0l} - \varphi_{le}$, then the set of evolution equations (15) can be written explicitly

$$\begin{aligned}\frac{\partial h_D}{\partial t} &= \gamma_D(\varphi_{0D} - \varphi_{1D}h_D + \varphi_{gD}h_g),\\ \frac{\partial h_g}{\partial t} &= \gamma_g\left(\varphi_{0g} - \varphi_{1g}h_g + \varphi_{2g}h_g^2 - \varphi_{3g}h_g^3 + \varphi_{gD}h_D\right).\end{aligned} \qquad (16)$$

The results obtained directly by integration of Eqs. (12) and via the effective potential approach (16) coincide if the relations $h_{ge} = (\varphi_{0g} - \varphi_{ge})/\varphi_{1g}$, $\varphi_{1g} \gg \varphi_{2g}h_{ge}$, and $\varphi_{1g} \gg \varphi_{3g}(h_{ge})^2$ between the coefficients of the internal energy presentations are fulfilled.

Setting the right-hand side of Eqs. (16) to zero, we get the equations for the stationary state

$$\begin{aligned}\varphi_{0D} - \varphi_{1D}h_D + \varphi_{gD}h_g &= 0,\\ \varphi_{0g} - \varphi_{1g}h_g + \varphi_{2g}h_g^2 - \varphi_{3g}h_g^3 + \varphi_{gD}h_D &= 0.\end{aligned} \qquad (17)$$

The first equation is linear in defect densities and therefore has a single solution. The second equation is cubic; it can have two stable solutions or two modes (at $\varphi_{gD} = 0$). A mode corresponding to a lower value of defectiveness describes a coarse-grained structure; a mode with higher defectiveness describes a fine-grained structure. The possibility of formation of several different modes of the same defect type is due to the microscopic mechanisms of deformation. In the case of grains this is because growth of the total surface area of GBs in the initial stage is an effective mechanism of energy dissipation. The contribution from triple junctions at this stage is negligible. The situation changes dramatically when the average size of grains decreases to about 100 nm. In this case, the triple junctions start to contribute considerably to the energy of boundaries, which may result in the formation of a new stationary state. Triple junctions can also be considered as a distinct defect type, but, since they are topologically attached to the grain boundary, it is more convenient to combine them with grain boundaries and consider them as a single defect type, but with a somewhat more complex dependence of its energy on their number.

The evolution of the system with the parameters from Table I is shown in Fig. 1. From Fig. 1(a) it is evident that the kinetics of grain boundaries and dislocations during the structural phase transition is closely correlated. At the first stage, a growth in the number of dislocations initiates the growth of grain boundaries and the structural phase transition. During the structural phase transition, when the density of

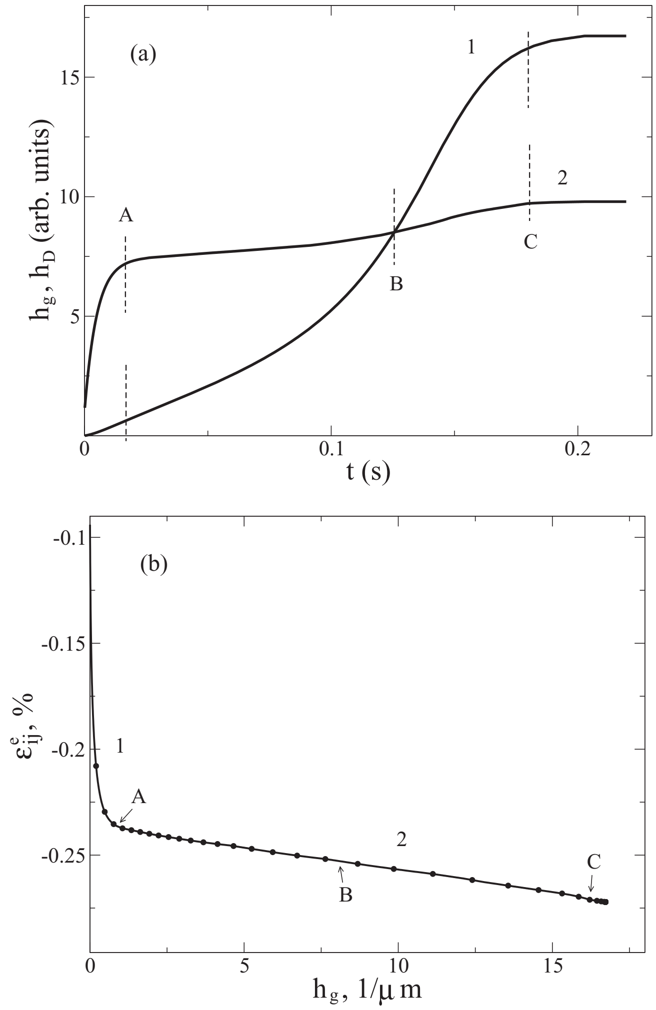

FIG. 1. Regularities of defect formation during SPD: (a) kinetics of defects: 1, density of grain boundaries; 2, density of dislocations and (b) unified strengthening curve: 1, region of the Hall-Petch law; 2, region of the linear law of strengthening. Points A–C highlight the formation of the most typical regions of kinetics and strengthening. Dots on the strengthening curve correspond to equal time steps.

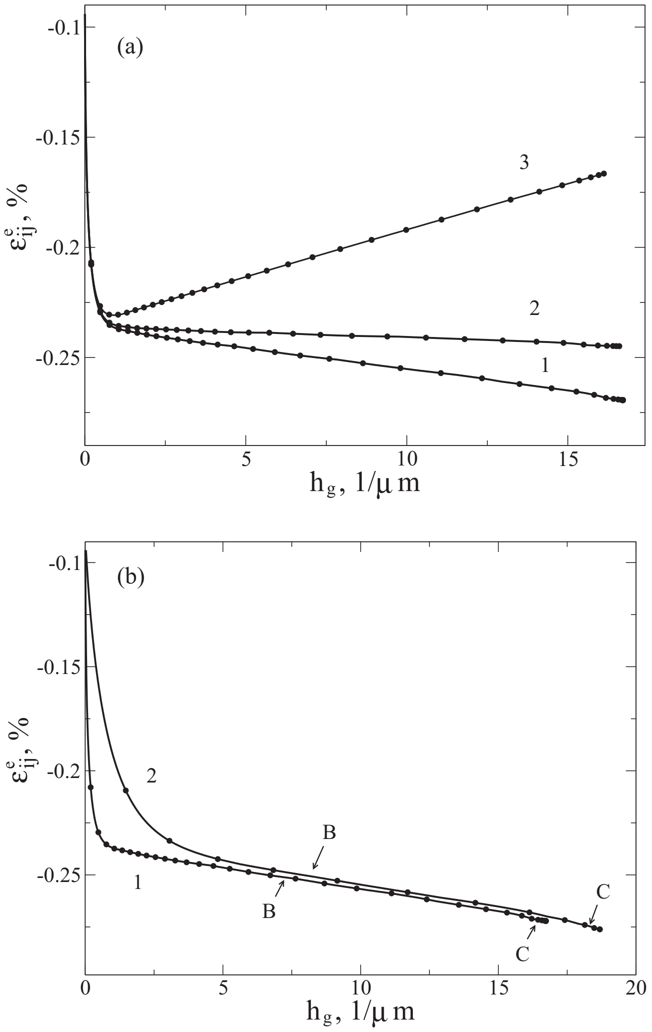

FIG. 2. Strengthening curves (a) including the effect of GB slip: 1, $w = 0$; 2, $w = 1.2 \times 10^{-11}$; 3, $w = 5 \times 10^{-11}$ and (b) with the parameter φ_{0g} increased 50 times: 1, $\varphi^*_{0g} = 0.4$ J m^2; 2, $\varphi^*_{0g} = 20$ J m^2; B and C are the same points as in Fig. 1.

dislocations is close to the stationary plateau, reciprocally, the growth of grain boundaries provokes the growth of the density of dislocations. Thus, in this range of deformations, dislocations follow the grain boundaries and repeat the shape of the structural phase transition curve, but to a weaker extent.

C. Strengthening curves

It is known that the strengthening comes from a dislocation mobility decrease due to breaking by various defects and by dislocations on other slip planes. At a dislocation level, the law of strengthening is described by the Taylor relation [64]

$$\tau = \alpha\mu b\sqrt{h_D}, \tag{18}$$

where τ is the shear stress, α is a coefficient taking values in the interval [0.2,1.0], μ is the shear modulus for a defectless solid, b is the Burgers vector, and h_D is the dislocation density.

If GBs are formed directly due to the emergence of dislocations, we can limit ourselves to the relation (18). The Hall-Petch law at the grain level follows immediately from that at the dislocation level.

In the present approach the elastic deformation is a control parameter, which, in the case of shear deformation, is related to stress by a simple dependence $\tau = \mu\varepsilon^e$. In terms of the present theory, the law of strengthening is

$$\varepsilon^e = \alpha b\sqrt{h_D}. \tag{19}$$

This dependence can be used as a supplemental relation to the energy and kinetic equations written above. Here for calculations it is assumed that $\alpha b = 2.75 \times 10^{-11}$ m$^{3/2}$.

The multistage character of deformation during SPD is also demonstrated by changes in the character of the strengthening law. At the first stage [region 1 to the left of point A in Fig. 1(b)] the law of strengthening can be approximated by the Hall-Petch law. In terms of the elastic deformations it is

$$\varepsilon^e = \varepsilon^{e0} + A\sqrt{h_g}, \tag{20}$$

where the constants are $\varepsilon^{e0} = 0.075$ and $A = 0.119$ mm. It can be seen that the elastic deformation varies within the limits of [0.1%,0.5%], which, in view of the value of the shear modulus, is well within the region of values for real materials.

In region 2 between points A and C, corresponding to the most rapid phase of SPD, the law of strengthening can be approximated by a linear dependence

$$\varepsilon^{e} = \varepsilon^{e1} + Bh_g \tag{21}$$

with constants $\varepsilon^{e1} = 0.27$ and $B = 0.0059\ \text{mm}^2$. A similar change of the strengthening law at different stages of deformation was noted in Ref. [65], which is discussed in Sec. III.

It is interesting to elucidate the influence of grain boundary slide on the above regularities. This requires taking more realistic (and complex) base relationships (18) and (19), including the weakening effect of sliding

$$\varepsilon^{e} = \alpha b\sqrt{h_D} - wh_g, \tag{22}$$

where w is the coefficient of weakening at the expense of the grain boundary sliding. The influence of this term is illustrated in Fig. 2(a).

The contribution of grain boundary sliding has almost no influence on the Hall-Petch region since its contribution is negligible at a low grain boundary density. At the same time, the sliding decreases the slope of the linear section (curve 2 in comparison to curve 1), which testifies to a lower material strengthening at this stage. At higher sliding the slope of the curve may change its sign (curve 3), which means that the material becomes weakened.

IV. DISCUSSION

The above simple two-defect model allows us to build the unified strengthening curve for the entire range of deformations, which contains both a section with the Hall-Petch law and a section with the linear law of strengthening. The two regions, i.e., the Hall-Petch strengthening law [33–35] and the linear law [39,40,66], have been considered separately in the literature. This is the main useful feature of the proposed model.

The important distinction of the proposed multidefect approach is that the defects at all levels are considered simultaneously. The evolution equations are written as a joint set of equations for all defect subsystems, whereas the traditional approach is based on sequentially solving a problem at one level and using the obtained results as model parameters for the next level [67,68]. The presented approach seems to be more natural in this regard.

Now there are questions as to whether the presented results are universal, how much they depend on the successful or unsuccessful combination of theory parameters, and what parameters are important. It is possible to assert that at the deformation stage with low defect density the main parameters are the coefficients standing at the lowest powers in the representation of the internal energy (10). For this stage Eqs. (16) can be significantly simplified

$$\frac{\partial h_D}{\partial t} = \gamma_D\varphi_{0D}, \quad \frac{\partial h_g}{\partial t} = \gamma_g\varphi_{0g}. \tag{23}$$

In accordance with these equations, the dislocations and GBs multiply independently of each other during this stage and their concentration grows linearly in time t,

$$h_D \sim \gamma_D\varphi_{0D}t, \quad h_g \sim \gamma_g\varphi_{0g}t. \tag{24}$$

Excluding time and using the Taylor relation (19), we get

$$h_g \sim \frac{\gamma_g\varphi_{0g}}{\gamma_D\varphi_{0D}}h_D = \frac{1}{\alpha^2b^2}\frac{\gamma_g\varphi_{0g}}{\gamma_D\varphi_{0D}}(\varepsilon^{e})^2, \tag{25}$$

which is the Hall-Petch law in its pure form

$$\varepsilon^{e} \sim \alpha b\sqrt{\frac{\gamma_D\varphi_{0D}}{\gamma_g\varphi_{0g}}}\sqrt{h_g}. \tag{26}$$

Thus, a section of the Hall-Petch law is not accidental on the strengthening curve; it reflects the fundamental features of the strengthening process that dislocations and GBs during this stage multiply independently of each other, but synchronously. Actually, (26) is a direct consequence of the Taylor relation (19).

Unfortunately, it is hard to obtain analytical solutions in other sections of the strengthening curve due to the inseparability of problem variables during integration. Therefore, it is impossible to confirm analytically the same conclusions in the linear section of the strengthening curve. However, this section is always present in a wide region of change of model parameters and it is the second fundamental feature of the strengthening process and of the defect accumulation during deformation.

The ratio between the length of the Hall-Petch section and the section of the linear strengthening one can be different. For example, increasing φ_{0g} ten times shortens the linear section [Fig. 2(b)]. Numerical calculations also show that an increase in the coefficient responsible for interconnection between the dislocation and the GB generation implies a similar result. Note in passing that the slope of the linear section is increased in this case.

On the basis of our analysis and generalization and the literary experimental data in Ref. [65] it is concluded that the nature of strengthening is changing from the Hall-Petch law at the initial stage of SPD, when the grains are large, to the linear law at the final stage of SPD with fine grains. A delimiting point for these strengthening laws in the case of an Armco iron sample is the state with a grain size of 0.4 μm, corresponding to $h_g \approx 2.5\ \mu\text{m}^{-1}$. Theoretical strengthening curves, presented above (namely, curve 2 in Fig. 2), are in full agreement with this conclusion.

V. CONCLUSION

In this paper two variants of the Landau-like approach were considered. The method of effective potential in terms of the internal energy is more convenient since it satisfies the extremal principle and allows one to obtain useful practical results. For the problem of grain structure refinement in metals, treated by severe plastic deformation, the unified stagelike strengthening curve over the entire range of deformation interval was obtained. At the initial stage the strengthening curve can be approximated by the square-root dependence, similar to the Hall-Petch law, and at the final stage it is a simple linear dependence.

The presented approach is thermodynamic and thus contains a large number of parameters. The values of some of them were estimated above, while some still remain uncertain. However, these parameters are not absolutely free. They are defined in the framework of a thermodynamic formalism, have clear physical meaning, and can be determined experimentally or from a suitable microscopic theory.

ACKNOWLEDGMENT

This work was supported by the budget topic 0109U006004 of the NAS of Ukraine.

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