Nonequilibrium evolution thermodynamic of poly- and two-components alloys affected by severe plastic deformation

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Abstract. The nonequilibrium evolutionary thermodynamics approach is generalized to the case of alloys prone to structural martensitic and diffusion phase transitions in them. A system of kinetic equations is written out to describe the evolution of the density of structural defects, grain boundaries, dislocations and point defects, as well as for the order parameter in the processing of these alloys by the severe plastic deformation way. The approach is illustrated by the numerical experiments results on a specific example of two-component copper-based alloys. Kinetic curves of the evolution of the grain boundaries, dislocations and atoms dissolved in a copper matrix are obtained, qualitative phase diagrams are constructed.

1. Introduction

Nonequilibrium evolutionary thermodynamics (NEET) describes defect formation during processing metals with polycrystalline structure by methods of severe plastic deformation (SPD) \cite{1, 2}. It is assumed that the phase state of the metal does not change or changes slightly. In most practically interesting cases this condition is fulfilled, but recently, alloys that are prone to structural phase transformations have been subjected to SPD treatment more and more often \cite{3-5}. Moreover, both the diffusion phase transformations of complex alloys, the balance of the processes of dissolution of the alloying component and the formation of nanocrystallites from it \cite{6}, and the diffusion less martensitic phase transformations \cite{7-9} are of interest.

In the simplest version, diffusion phase transitions are studied experimentally on two-component systems based on copper doped with cobalt \cite{10}, silver or tin \cite{11}. The phase diagrams of such alloys are well studied. Of particular interest is the processing of such alloys by SPD methods, in particular, during high pressure torsion (HPT) \cite{10, 11}. Using the example of CuCo and CuAg alloys, experiments show that from any point in the phase diagrams, with a sufficient number of revolutions (in the asymptote), the material always comes to a single universal stationary state. Moreover, if the initial density (concentration) of the dissolved atoms is lower than the stationary value, then it increases during the SPD, and, conversely, if it is higher, it decreases.

For a full theoretical solution of the problem, it is necessary to consider two sub-problems. Within the framework of the theory of phase transitions, describe the equilibrium phase diagram, which is achieved as a result of annealing samples, and then, using these equilibrium states as initial data, to calculate the system state evolution during SPD. Some preliminary attempt to solve these two parts of the problem was made in the works of the authors \cite{12}, in which it was assumed that there is a certain order parameter that is responsible for the interplane distance in an alloy. On the equilibrium line of the phase diagram, the system experiences a first order phase transition, after which it begins to be
saturated with the dissolved component Ag, Sn, or others, and which until this moment was concentrated compactly in particles inside the copper matrix.

Second feature of the model is that the spatial Lifshitz invariants multiplied by the modulus of the external mechanical torque are used to describe the twisting of the alloy during the HPT. The applicability of these invariants is limited, however, to materials in which there is no inversion center, and it is very problematic in the general case. However, it can be assumed that in the general case, the external mechanical torque violates the central symmetry of the material, therefore, in the bundle of the product of the modulus of the mechanical torque by the Lifshitz invariant, this idea seems quite correct. At the same time, the Fourier transform is actually used to account for spatial inhomogeneity, which reduces the problem to a homogeneous variant, but in this case, by selecting the model parameters, the Lifshitz invariants can be eliminated altogether.

In this paper, we will limit ourselves to solving only the second part of the problem within the framework of the NEET, and we will postpone the refinement of the model for the first part to a later time.

2. General solution of the problem

In this chapter a variant of NET for multicomponent alloys is presented, taking into account the influence of structural defects. The dynamics of defects can be divided into two categories: 1 - generation and annihilation of all types of structural defects, including point ones, during SPD, and 2 - thermal relaxation of defects before and after SPD. At the second stage, only point defects relax completely to the equilibrium state, and other more powerful defects, dislocations and grain boundaries (GB), relax only a little, reducing their length (curvature) or area to a certain minimum size, but the general topological grid remains unchanged, and it can be in principle any achievable with this method of processing.

In this regard, the main idea of the improved NEET method is that in order to take into account possible martensitic phase transformations (PT) during SPD, it is necessary to introduce order parameter (OP) into the internal energy. To do this, it is better to start from the expression of free energy and go through the transformation $U = F + TS$ to the internal energy, and then according to the standard NEET scheme, in which the OP will also evolve, as well as the density of defects. For diffusive PT, it is also necessary to take into account the heterogeneity of the problem for all types of defects and for OP too (in the form of domain boundaries movement).

The internal energy density $\nu$ in this NEET paradigm for a homogeneous problem, in addition to the classical defects for SPD, GB and dislocations, also includes point defects, for example, vacancies and interstitials, and may also include components of an alloy, compound or solution. In this formulation, the internal energy density due to the subsystems of the defects has the form

$$\nu = h_0 + \sum_{l=P,D,G} (\varphi_0 h_0 l^2 - \frac{1}{2} \varphi_1 h_1 l^3 + \frac{1}{3} \varphi_2 h_2 l^4 - \frac{1}{4} \varphi_3 h_3 l^5) + \nu_{\text{interact}}, \quad (1)$$

where $h_l$ – densities of structural defects, point defects $l = P$, dislocations $l = D$ and grain boundaries $l = G$ in this example, $\varphi_{kl}$, – energetic coefficients of the theory. The last term describes linear and nonlinear interactions between defects of various types, as well as interaction with alloy components.

It is assumed that in the case of diffusion-free martensitic transitions, the component composition does not change during SPD, but the structural organization of the alloy or compound may change. This can be taken into account by introducing the known invariants by the order parameter into the internal energy (1). For certainty, we consider the Heusler alloy, although the technique considered here is suitable for any alloy experiencing a martensitic phase transition. The structural part of the free energy density for it already in some simplified version has the form
where $e_2$ and $e_3$ – the shear and dilatation component of the deformation (secondary OP), which are associated with the strain tensor

\[
e_2 = \left( e_{xx} - e_{yy} \right) / \sqrt{2},
\]

\[
e_3 = \left( 2e_{zz} - e_{xx} - e_{yy} \right) / \sqrt{6}.
\]

If we are not interested in the multivariance of the martensitic phase, then in the free energy (2) we can put $e_2 = 0$

\[
f_s = f_0 + \frac{1}{2} ae_2^2 + \frac{1}{3} be_3^3 + \frac{1}{4} ce_3^4 + \sigma e_3,
\]

where the term responding for interaction between OP and external stress $\sigma$ is added.

According to Landau, the temperature dependence is carried out through a coefficient at the second power of OP in the form

\[
a = a_0 (T - T_M),
\]

where $a_0$ is some new constant, $T_M$ is the critical temperature of the martensitic transition. The coefficient critically depends on the temperature, changes its sign when the temperature passes through the point $T_M$. But other coefficients can also depend on the temperature, maybe not in a critical way. All the coefficients of the free energy in principle can also depend on external stresses. Since the thermodynamic potential (2) contains a cubic term relative to the structural OP, the martensitic phase transition will be of the first order.

The structural entropy density associated with OP can be found from the expression

\[
s_{op} = -\frac{\partial f}{\partial T} = s_0 - \frac{1}{2} \frac{\partial a}{\partial T} e_2^2 - \frac{1}{3} \frac{\partial b}{\partial T} e_3^3 - \frac{1}{4} \frac{\partial c}{\partial T} e_3^4.
\]

If we limit ourselves to the linear dependence of the coefficients $b$ and $c$ on temperature

\[
b = b_0 + b_1 T,
\]

\[
c = c_0 + c_1 T,
\]

then (5) take the form

\[
s_{op} = \frac{1}{2} a_0 e_2^2 + \frac{1}{3} b_0 e_3^3 + \frac{1}{4} c_0 e_3^4 + \frac{1}{2} a_1 (e_2^2 + e_3^2) + \frac{1}{3} b_1 e_3^2 - 3e_3 e_2 + \frac{1}{4} c_1 (e_2^2 + e_3^2),
\]

and in an explicit form, the structural part of the entropy does not depend on temperature.

It is interesting to note that the dependence of the structural entropy on the PP has exactly the same character as the free energy (2) only with other coefficients. Based on this, the structural entropy can be divided into the sum of terms proportional to the invariants of OP

\[
I = e_2^2 + e_3^2,
\]

\[
I_2 = e_3^2 - 3e_2^2,
\]

and their powers, namely
\[
s_{OP} = \frac{1}{2} a_1 I_1 + \frac{1}{3} b_1 I_2 + \frac{1}{4} c_1 I_1^2. \tag{9}
\]

Or, denoting
\[
s = \frac{1}{2} a_1 I_1,
\]
\[
s = \frac{1}{3} b_1 I_2,
\]
instead of (9), we get
\[
s_{OP} = s + A s^2_1.
\tag{11}
\]

where
\[
A = \frac{c}{a}. \tag{12}
\]

Here \(s_I\) is a part of the structural entropy, the internal source of which is the loss of orderliness in the form of the invariant \(I_1\) during the transition to a more symmetric phase, and, conversely, its sink when orderliness appears during the transition to a lower symmetric phase. Accordingly, \(s_2\) is a part of the structural entropy, the internal source of which is the loss of orderliness in the form of the invariant \(I_2\). The first two terms in (11) are the expansion of structural entropy according to its sources associated with a change in the symmetry of the crystal in the linear approximation, and the last term in the quadratic one.

If the temperature dependence of the coefficients \(b\) and \(c\) can be neglected, then the expression (5) is simplified
\[
s_{OP} = -\frac{1}{2} a_0 \left( e_2^2 + e_3^2 \right). \tag{13}
\]

The entropy \(s_{OP}\) plays the role of the configuration entropy for the OP. The part of the internal energy density due to OP for the case (7) will be equal to
\[
u_{OP} = f + Ts_{OP} = f - \frac{1}{2} a T e_0^2 + \frac{1}{3} b e_0 e_2 e_3 + \frac{1}{4} c \left( e_2^2 + e_3^2 \right)^2. \tag{14}
\]

As one can see, this part of the internal energy does not explicitly depend on temperature. The internal energy as a whole will consist of the sum of the internal energies of the defects subsystems and the structural part, and also include the energies of all interactions \(u_{interact}\)
\[
u \left( h_p h_D h_g e_2 e_3 \right) = u \left( h_p h_D h_g \right) + u_{OP} \left( e_2 e_3 \right) + u_{interact}. \tag{15}
\]

To the usual system of evolutionary equations of the NEET for structural defects
\[
\frac{\partial h}{\partial t} = \gamma_P \left( \varphi_{OP} - \varphi_{OP-P} h + \varphi_{DP} h + \varphi_{OP-P} OP \right) + f_P. \tag{16}
\]
it is necessary to add the evolutionary equations for $O_P$,

\[ \frac{\partial h}{\partial t} = \gamma_D \left( \frac{\partial}{\partial 0_D} - \frac{\partial}{\partial h} + \frac{\partial}{\partial h_D} \right) + f_D, \quad (17) \]

\[ \frac{\partial h}{\partial t} = \gamma_g \left( \frac{\partial}{\partial 0_g} - \frac{\partial}{\partial h} + \frac{\partial}{\partial h_g} - \frac{\partial}{\partial h^2} + \frac{\partial}{\partial h^3} + \frac{\partial}{\partial h_P} + \frac{\partial}{\partial h_{OP-D}} \right) + f_g, \quad (18) \]

Thus, a system of consistent formulas and relations is obtained, in which it is assumed that possible phase transitions of the martensitic and/or diffusion type are described during the processing of alloys during severe plastic deformation.

3. Non-stationary problem

Using equations (16) – (19), it is possible to calculate the joint evolution of structural defects and order parameters. An important fundamental feature of this evolution is the presence of a certain universal stationary state, to which the system tends in the process of evolution. For example, if the initial density of the alloying component in the alloy is lower than its stationary value, then the density of the component increases, if higher, it falls (Figure 1). This pattern was observed in the experiment for the Cu-Co alloy (See Figure 1 in [10]).

**Figure 1.** The evolution of the density of atoms of the alloying component during SPD. 1 – the initial density is higher than the stationary value, 2 – the zero initial value of the density of the alloying component.

**Figure 2.** The evolution of the densities of grain boundaries (1), dislocations (2) and the alloying component (3) during SPD. Fine lines refer to the case of a pure Cu matrix.

However, due to limited technical capabilities, it is difficult for experimenters to carry out the entire range of measurements at once, including measurements of the densities of structural defects. Theoretically, it is not difficult to do this, and Figure 2 shows the results of such calculations. The parameters of the model for comparability with the previously performed calculations were chosen to coincide with those for pure material given in [1]. The thin dotted lines refer, precisely, to the case of a pure matrix. The possibility of dissolution of the alloying component leads to a time delay in the evolution of grain boundaries and dislocations. This can be explained by the fact that the work of
external stress branches off to the dissolution of the alloying component, as a result of which the formation of structural defects slows down.

4. Diagrams of state for two-component alloys

The second important point of the theory of diffusion phase transitions is related to the construction of temperature phase diagrams of two-component alloys without and with SPD. To achieve an equilibrium state at a particular temperature, the alloy is subjected to prolonged annealing at this temperature [11]. As a result, an equilibrium distribution of dissolved atoms is formed in it, and the temperature dependence of the equilibrium curve had a certain non-monotonic character (see Figure 1 in [11]). This curve can be calculated in the framework of the classical theory of diffusion phase transitions, consistent with the NEET. Since we do not address this issue in this article, it is appropriate to construct simplified qualitative diagrams for such alloys. Since only the initial value of the density of the dissolved component is important for the SPD process, we can replace the uniform temperature scale with a uniform scale of the density of this component (vertical axis), the temperature scale according to the experimental phase diagram in this case will be uneven (Figure 3, 4). The horizontal axis in these figures will reflect the change in the density of the dissolved component during the SPD. For this reason, the line 0 corresponding to the initial values of the density of the dissolved component will go on the graph at an angle of 45 degrees (Figure 3, 4).

As one can see, during the processing of alloys by SPD methods, at a sufficiently high level of plastic deformation, all alloys reach a certain universal state, regardless of the initial state from which the SPD processing started (line 2 in Figure 3 and line 1 in Figure 4). If the degree of deformation is not high enough, then the system does not reach a universal state and comes to some intermediate state (inclined line 1 in Figure 3).

At the same time, it can be seen from Figure 1 that the system can, in principle, have not one, but at least two universal stationary states. This indicates that the state of the system as a whole depends not only on the dissolved component, but also on structural defects. And it is well known that such structural defects as grain boundaries can have a two-mode distribution [13-15], which is associated
with the possibility of having two maxima in the nonequilibrium thermodynamic potential [2]. The first maximum in the area of large grain size is associated with the grain boundaries themselves, and the second maximum is associated with the presence of triple joints or disclinations. At the same time, the disclinations in the NEET are taken into account not as a separate independent defect, but through the “renormalization” of the energy of the grain boundaries [2]. When during "annealing" the density of structural defects increased with an increase in the initial density of the dissolved component, as was assumed in the computer experiment, it is possible to get into both stationary states below and above the intersection point of lines 0 and 2 in Figure 3. If the density of structural defects was the same for all “annealing”, then the system reached the same stationary state for all initial values of the density of the dissolved component (Figure 4).

To obtain greater similarity with the experimental results of [11], we introduce an experimental curve as the initial density distribution of the dissolved atom, and we model the output to the stationary state from the NEET equations (Figure 5). In this case, the vertical scale is expressed in temperature scales. The development of a theory for calculating the equilibrium annealing curve, consistent with the NEET, is still under consideration.

![Figure 5](image.png)

**Figure 5.** Phase diagram of the alloying component $h_L$ during SPD. 0 – experimental annealing curve of the alloy, 1 – stationary state.

### 5. Conclusion

As part of the generalization of the method of nonequilibrium evolutionary thermodynamics to alloys, taking into account the possibility of structural martensitic and diffusion phase transitions, a system of kinetic equations is obtained to describe the evolution of the densities of the main structural defects and the order parameter under conditions of severe plastic deformation. It has been established in computer experiments that under such conditions the system always tends to some one or two universal stationary states.

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