

Scenarios of Nonequilibrium Phase Transformations in Alloys Depending on the Temperature and Intensity of Plastic Deformation

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Abstract—Based on analyzing experimental data and existing theoretical approaches, this study has formulated concepts of regular change in scenarios of phase transformations developing under severe plastic deformation. Depending on the temperature and other deformation conditions, the mechanical energy supplied to the system can dissipate by various routes (dislocation glide, dynamic recrystallization, grain structure refinement, disordering, amorphization, and diffusion redistribution of alloy components), giving rise to a diversity of observed phase and structural states. A diagram of nonequilibrium states of alloy as a function of conditions of severe plastic deformation has been proposed. The applicability of the presented concepts has been demonstrated for a wide range of alloys and compounds.

Keywords: plastic deformation, nonequilibrium phase transformations, mechanical alloying, nanocrystalline materials, dynamic recrystallization

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1. INTRODUCTION

Unusual structural and phase transformations in alloys under severe plastic deformation (SPD) have attracted much attention in recent decades [1–10] in the context of developing new materials. A common feature of a large group of transformations, which at first glance differ significantly in physical nature (disordering and amorphization of intermetallics [1, 8], mechanical alloying in immiscible systems [9–15], dissolution of phase precipitates [2, 16–20], decomposition with precipitation of nonequilibrium phases [21, 22], formation of stable patterns [23], and cyclic reactions [24–26]), is the fact that the alloy under SPD recedes from the thermodynamic equilibrium state. This means that the mechanical energy supplied to the alloy partially converts to the internal energy of the alloy. On completion of the treatment, the reached nonequilibrium state of the alloy remains “frozen.”

Although numerous works have been published on the subject, there is limited comprehension of the picture of phase transformations under SPD. This is likely due to the fact that plastic deformation is a complex multilevel process, which, depending on the temperature and intensity of deformation, occurs by different microscopic mechanisms. Although mechanisms of phase transformations under SPD and/or during subsequent annealing have been discussed in recent decades [1–10], the problem of classifying such transformations and determining the main mechanisms by

which they occur, depending on external conditions, remains an urgent one.

Based on analyzing experimental data and existing theoretical approaches, we proposed in this work a diagram of nonequilibrium structural and phase states, which can form a conceptual basis for classifying anomalous transformations under SPD.

2. MECHANISMS OF ANOMALOUS PHASE TRANSFORMATIONS

At elevated temperatures ($T > 0.5T_m$, where T_m is melting point) under SPD, diffusion promotes transformations after which the system becomes closer to the equilibrium state, whereas at temperatures below room temperature, direct atomic mixing in deformation bands probably dominates. During long-term treatment this ensures the disordering of intermetallics and mechanical alloying even in immiscible systems [9]. After disordering, the amorphous state can form if it is energetically more favorable than the disordered state [8]. At the same time, debate continues on mechanisms of transformations within the intermediate temperature range $(0.3–0.5)T_m$, where diffusion and direct mechanical mixing compete with each other.

Experiments showed that the vacancy concentration under SPD reaches premelting values of $\sim 10^{-3}$ [27, 28], accelerating diffusion by 5–15 orders of magnitude and causing, e.g., phase separation of alloys

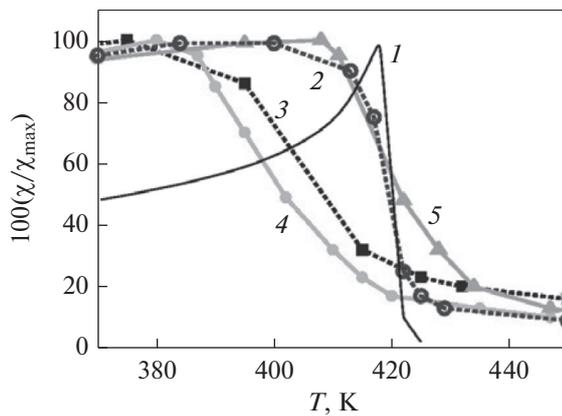


Fig. 1. Magnetic susceptibility of (1) the initial homogeneous alloy $\text{Ni}_{40}\text{Pd}_{60}$ and its sample after treatment in a ball mill at (2) 80, (3) 300, (4) 403, and (5) 523 K [34].

[29] or decomposition into pure components (according to the equilibrium phase diagram) even at room temperature [7]. At the same time, estimates of the decomposition rate in the systems Al–Mg [30] and Cu–Ni [31] suggested that the acceleration of diffusion by generation of nonequilibrium vacancies is insufficient; therefore, we can assume that decomposition is controlled by diffusion via structural defects (dislocations, grain boundaries). The grain-boundary diffusion of Co in Mo under SPD using high-pressure torsion was studied by layer-by-layer radiometric analysis [32]. We determined that under SPD, nonequilibrium grain boundaries formed, which were paths of ultrafast diffusion (3–5 orders of magnitude faster than diffusion via ordinary grain boundaries). The state of grain boundaries in ultrafine-grained W and Mo samples produced under SPD using high-pressure torsion was investigated by emission Mössbauer spectroscopy [33]. The treatment was shown to give rise to nonequilibrium grain boundaries, which were characterized by an excess free volume formed probably by delocalization of lattice dislocations arriving at grain boundaries.

Such examples as the anomalous phase separation in the Ni–Pd system of mixed components (detected by a shift of the Curie temperature after deformation, Fig. 1) [34] or the decomposition of the equilibrium tetragonal phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ into an amorphous phase enriched in Nd and α -Fe nanocrystals [21, 22] clearly demonstrate that, under SPD, nonequilibrium diffusion-controlled transformations can occur. In this context, the question arises of the possible role of diffusion in disordering of alloys and formation of supersaturated solid solutions, i.e., in nonequilibrium phase transformations that are most typical under SPD but usually regarded as diffusionless.

It is generally believed that mechanical mixing under SPD occurs by numerous shears in intersecting slip planes. As a result, in the initially ordered alloys,

antiphase boundaries are accumulated and the alloys are disordered, and in alloys containing precipitates, there are precipitate refinement and dissolution [9, 35]. At low temperatures, when diffusion processes are suppressed, mechanical mixing during continuing treatment develops irreversibly. At moderate temperatures, in systems that are thermodynamically prone to decomposition, atomistic simulation demonstrates the formation of modulated structures (patterns) as a result of the competition of mixing and diffusion [36, 37], which agrees with the experimental data on the Ag–Cu system [23]. It was proposed [9, 35] to consider mixing under SPD by analogy with the ballistic mechanism of mixing under irradiation [38, 39] and postulated that neighboring atoms are exchanged at a frequency that depends on the treatment intensity, rather than on temperature. The main conclusion [9, 35] is that, under the action of kinetic factors (ballistic mechanism), the representative point of the alloy effectively shifts upward along the temperature axis in the equilibrium phase diagram. In these terms, the experimentally observed phenomena of disordering [7] and formation of supersaturated solid solutions [7] were qualitatively explained.

However, the universality of this approach is challenged by a number of experimental data and theoretical estimates. First, the formation of supersaturated solid solutions is accelerated in the nanocrystalline state [13, 14], where the dislocation glide in the bulk of the grains is suppressed [40, 41], and hence the proposed [9] direct-mixing mechanism is impossible. Second, it was reported [4, 42] that, in most experiments, mechanical alloying begins with the formation of solid solutions and intermetallics based on a low-mobility component, which is clearly indicative of diffusion control of the transformation. And third, the phenomenon of diffusion dissolution of precipitates of equilibrium phases in the course of their cutting by dislocations has been reliably established experimentally [2] and can be explained within the framework of the theory of so-called “diffusion cutting” [43].

It has been shown recently [16, 17] that particles of the Ni_3Ti and Ni_3Al phases in austenitic steel, which were previously assumed to dissolve by diffusion cutting, dissolve more efficiently at low temperatures, down to 77 K (Fig. 2). It was hypothesized that, in this case, diffusion cutting by dislocations occurs not by the vacancy-driven diffusion mechanism, but, more likely by the crowdion diffusion mechanism, which has lower activation energy and is therefore preferable at low T . It was previously stated, based on estimates of the change in the average lattice parameter under SPD, that the concentration of interstitial defects under SPD can reach 1 at. % [4].

In constructing a consistent picture of anomalous phase transformations under SPD, the main problem therefore is to reveal microscopic mechanisms of these transformations and analyze their change depending

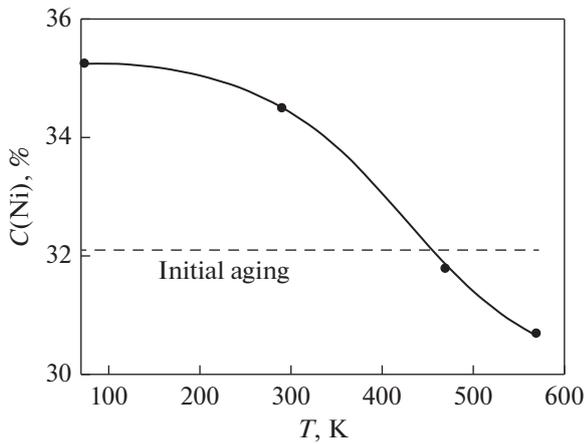


Fig. 2. Dependence of the Ni concentration (at %) in the matrix of the austenitic alloy Fe–36Ni–9Al preliminary aged at 873 K on plastic deformation temperature (shear under the pressure $P = 8$ GPa). The dashed line indicates the initial Ni concentration in the alloy [17].

on external conditions (temperature, pressure, and intensity of treatment). Significant factors in these mechanisms are accelerated diffusion via structural defects (dislocations and grain boundaries), local change in thermodynamic properties of alloy near the cores of structural defects, motion of dislocations and grain boundaries under SPD, direct mechanical mixing by numerous shears in intersecting planes, and generation of nonequilibrium point defects (vacancies and interstitial atoms).

3. DIAGRAM OF NONEQUILIBRIUM PHASE TRANSFORMATIONS UNDER SEVERE TREATMENT

Here, we systematize the observed picture of phase transformations under SPD within an approach that uses general principles of nonequilibrium thermodynamics [44, 45]. Under deformation, external forces do work on a system, and the energy supplied to the system is spent on heat production, generation of defects, and change in the free energy of the alloy, i.e. on its distance from the thermodynamic equilibrium state:

$$W = \frac{dH}{dt} - T \frac{dS}{dt} + \frac{dE_{\text{def}}}{dt} + q, \quad (1)$$

where W is the energy supplied to the system per unit time; H and S are the enthalpy and entropy of the alloy, respectively; E_{def} is the energy of defects; and q is the heat released in the system per unit time. Expression (1) is more general than that proposed previously [46], which took into account only the energy of defects and ignored the change in H and S during the development of nonequilibrium transformations. After reaching a steady-state mode, the energy sup-

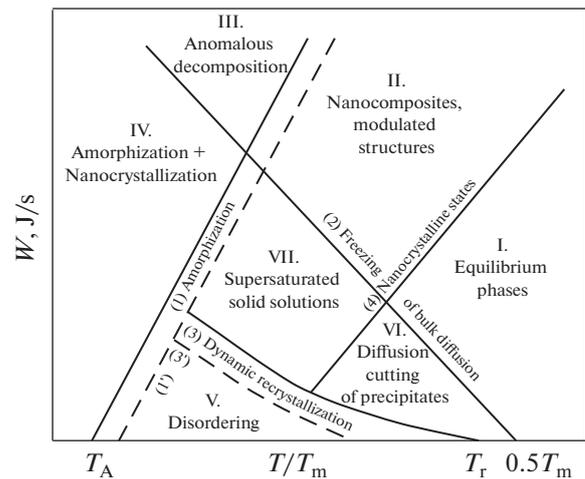


Fig. 3. Diagram of nonequilibrium phase states of alloy under severe phase deformation.

plied to the system per unit time is equal to the heat released, which is discharged to the environment: $W = q$. The state of the alloy is characterized by nonequilibrium steady-state quantities $H(T, W)$, $S(T, W)$, and $E_{\text{def}}(T, W)$, which depend on temperature T and treatment intensity W . The alloy under SPD is therefore a classical dissipative system [45].

Under deformation treatment, at grain boundaries and triple junctions, plastic incompatibilities (partial disclinations—mesodeflects of the rotational type) are accumulated, which are sources of powerful elastic stresses [40, 47–49]. We can regard the emerging nonequilibrium states of the alloy as a result of the dissipation of this elastic energy via available routes of structural relaxation (plastic deformation, grain structure refinement, amorphization, dynamic recrystallization, generation of nonequilibrium point defects). The conditions of switch of the elastic energy dissipation mechanisms depend on many factors (temperature, pressure, total strain, strain rate, grain size, etc.). We chose the rate W of supply of mechanical energy to the system as the main control parameter. The second important parameter is temperature T , which determines the rate of relaxation processes. Note, however, that, if SPD is performed at high pressure, then the treatment may give rise to high-pressure equilibrium phases (including little-known low-temperature ones) [50].

Figure 3 presents a schematic diagram of nonequilibrium states of alloy that are reached by nonequilibrium phase transformations under SPD. Characteristic lines of the diagram in the homological temperature T/T_m —treatment intensity W coordinates are conditional, but their relative positions qualitatively agree with known experimental data.

Line (1) of the beginning of amorphization has a positive slope because, for transition to the amorphous state at elevated temperature, a higher energy flux

should be supplied to the alloy to prevent thermally activated structural relaxation processes. Indeed, we assumed [8] that amorphization is a consequence of mechanically driven disordering of alloys and intermetallics and occurs if the amorphous state is energetically more favorable. In this case, crystal order restoration is activated with short-range diffusion. In the limit of low treatment intensities ($W \rightarrow 0$), one can conditionally indicate critical amorphization temperature ($T_A \sim 300$ K), on cooling to which the short-range (on the order of the lattice parameter) bulk diffusion becomes negligible, so that the restoration of the initial ordered state becomes impossible. With decreasing average grain size, the line of the beginning of amorphization can shift to the right ($(I) \rightarrow (I')$) because the grain boundaries contribute to the total energy of alloy (it is known, e.g., that the irradiation-induced amorphization of nanocrystalline samples is faster than that of coarsely crystalline ones [51]).

Line (2) of freezing of bulk diffusion characterizes the conditions under which we can neglect long-range diffusion necessary for phase transformations specified in the equilibrium phase diagram that are accompanied by changes in chemical composition (decomposition into phases, dissolution of precipitates). The line has a negative slope because SPD leads to generation of nonequilibrium point defects, accelerating the bulk diffusion by 5–15 orders of magnitude [27, 28]. Under normal conditions, bulk diffusion can usually be neglected at $T/T_m < 0.5$.

Line (3) of the beginning of dynamic recrystallization also has a negative slope [46]. As recrystallization is controlled by short-range diffusion and grain-boundary diffusion, lines (2) and (3) generally do not coincide. For example, in the Fe–Cu system under deformation by torsion at high pressure, ~~we observed~~ dynamic recrystallization even at $T = 77$ K [52]. In the limit of low treatment intensities ($W \rightarrow 0$), the dynamic recrystallization temperature tends to the temperature T_r of the beginning of static recrystallization, which, depending on the composition of the material and the strain, can be both lower and somewhat higher than $0.5T_m$. Line (3') expresses the fact that, with decreasing grain size, the temperature T_r and, consequently, the line of the beginning of dynamic recrystallization shift to the left.

A concept was proposed [46] that low-temperature dynamic recrystallization plays an important role as a mechanism ensuring transition to the nanocrystalline state because conventional mechanisms of plastic deformation (dislocation mode and rotational mode) degenerate with decreasing grain size to 200 nm [40].

One of the routes of the dissipation of the energy supplied to the system is grain structure refinement. A significant role is played by line (4) dividing the regions of nano- and polycrystalline states. A hypothesis of the existence of a steady-state grain size depending on the temperature and rate of deformation

has long existed [53] and has reportedly been confirmed experimentally [54]. Under SPD, the nanocrystalline state is qualitatively different from the polycrystalline one, in particular, by the state of grain boundaries. So-called nonequilibrium grain boundaries [55] emerge, near which the crystal structure of the material is strongly distorted and is characterized by high stored elastic energy (and, likely, high structural disorder, depending on the type of boundaries). We drew line (4) parallel to line (1) of the beginning of amorphization, assuming that transition to the nanocrystalline state precedes amorphization. Line (4) ends at line (3) of the beginning of dynamic recrystallization according to the concept [46] that low-temperature dynamic recrystallization is a necessary condition of transition to the nanocrystalline state.

Let us now discuss the types of phase transformations that we expect in various sectors of the constructed diagram.

In sector I, there are phases specified in the equilibrium phase diagram. Due to the acceleration of diffusion, the sector expands toward lower temperatures, where the treatment allows us to obtain low-temperature phases that are difficult to produce using other treatment methods. In particular, even at room temperature, we could observe decomposition with precipitation of equilibrium phases in such systems as Ni–Cu [31, 56], Cu–Co [7], and Fe–Ni [57]. In the Fe–Ni–Al alloy under SPD in Bridgman anvils at $T = 573$ K, accelerated precipitation of particles of the equilibrium phase Ni_3Al occurred, whereas, conversely, the treatment at $T = 77$ – 473 K led to the dissolution of such particles [58].

In sector II, equilibrium transformations develop in the presence of a large number of defects, in particular, grain boundaries, in the course of competing processes of mixing, dynamic recrystallization, and efficient grain structure refinement. Nanocomposites of small grains of immiscible components can form here. For example, ~~we detected~~ modulated structures in the Ag–Cu system under SPD at moderate temperatures ($T > 450$ K), whereas the homogeneous state was reached [23] at lower temperatures.

In sector III, the competition is between amorphization (typically observed in intermetallics and ordered alloys) and bulk diffusion. As atomic order restoration is controlled by short-range diffusion, reaching the amorphous state requires high treatment intensity. In the presence of amorphous phases, the conditions of thermodynamic equilibrium change, which may lead to the formation of anomalous (non-equilibrium) crystalline phases in the course of the treatment. An example of a transformation of this type is the decomposition of the equilibrium tetragonal phase $Nd_2Fe_{14}B$ into an amorphous phase enriched in Nd and α -Fe nanocrystals, which ~~we~~ observed under SPD by shear under the pressure 5–11 GPa in Bridgman anvils [21, 22]. In mechanical alloying of a mix-

ture of powders of Fe, Cr, and graphite in a ball mill, the phase composition of the final product and the presence of carbides in it was likely to be determined by the dynamic equilibrium between crystalline phases and an amorphous phase [59]. Another example is the $\text{Fe}_{50}\text{B}_{50}$ system, in which in the equilibrium state the intermetallic FeB formed. At high intensity of the treatment of a mixture of powders of Fe and B in a ball mill, we detected nonequilibrium phases based on Fe and B and the amorphous phase Fe–B [60], and at lower intensity the disordered solid solution Fe–B formed [26, 61]. The transition between two possible nonequilibrium states in this system should correspond to a shift of the representative point from sector III to sector IV in the presented diagram.

In sector IV, bulk diffusion is frozen, and the observed transformations are determined by the competition of amorphization and the possible nanocrystallization, with the latter being an ~~additional~~ mechanism of return to the equilibrium (ordered) state. In this sector, in particular, the amorphization–nanocrystallization cyclic reaction occurs, which ~~we~~ detected in the Co–Ti system [24, 25].

At sufficiently low temperatures, in this sector of the diagram, both bulk diffusion and nanocrystallization are suppressed; therefore, disordering and amorphization of alloy are the main routes of the dissipation of the energy supplied to the alloy. Prior to amorphization, because there is no dynamic recrystallization, plastic deformation occurs by passage of dislocations through the bulk of the grains. The domination of the dislocation mode of plastic deformation in this sector agrees with the proposed [9] mechanism of disordering by passage of dislocations the Burgers vector, which differs from the lattice translation vector. We obtained most experimental data on the amorphization of alloys under SPD at temperatures no higher than room temperature [1, 8], and, moreover, ensuring high treatment intensity and reaching small grain size are generally not required, which agrees with the proposed diagram.

In sector V, bulk diffusion and dynamic recrystallization are suppressed, and the condition of the beginning of amorphization is not reached. In this case, we should expect a weak influence of SPD on the structural state, which is particularly seen in partial disordering in ordered alloys. However, according to this concept [46], the nanocrystalline state is not reached below line (3) of the beginning of dynamic recrystallization, and, hence, plastic deformation in this sector occurs in the dislocation mode. Then, in this sector, in long-term treatment, one could expect mechanical alloying by the previously proposed [9] mechanism, i.e., via refinement of precipitates of phases by numerous shears. However, in most cases [10], mechanical alloying is activated by transition to the nanocrystalline state (sector VII), where the dislocation mode of

plasticity is suppressed [40], which disagrees with the proposed [9] concept of mechanical alloying.

In sector VI, bulk diffusion is frozen, but there is diffusion on dislocations and grain boundaries, which can be sufficiently mobile. In this sector, there are optimal conditions for local dissolution of precipitates by their diffusion cutting by moving defects (dislocations and grain boundaries) [43]. Indeed, experiments demonstrated diffusion cutting by dislocations, specifically, diffusion cutting of γ' particles of Ni_3Al in the alloy 75Ni–19Cr–6Al (at. %) [62], particles of intermetallics in the Fe–Ni–Ti austenitic alloy [63], and particles of carbides in steels [64].

Finally, in sector VII, dynamic recrystallization favors the formation of the nanocrystalline state [46], and there are neither bulk diffusion nor amorphization. It was stated [40] that, in the nanocrystalline state, the dislocation mode of plasticity is also suppressed. At the same time, grain-boundary diffusion may remain significant, stimulating the development of nonequilibrium segregations or the decomposition of alloy in the boundary region. According to experimental data, it is in this sector of the diagram (i.e., on reaching the nanocrystalline state), that the formation of supersaturated solid solutions in mechanical alloying is most often observed [10], which may indicate the important role of grain boundaries and dynamic recrystallization in this process.

4. TRANSFORMATIONS IN THE Mn–Al–C ALLOY

Let us illustrate the proposed concept of nonequilibrium phase transformations under SPD using the example of the Mn–Al–C alloy, which was the object of extensive experimental investigations at various temperatures and intensities of treatment in a ball mill [65–67]. A feature of this system is the fact that, on cooling from the high-temperature state to a temperature $T < 1110$ K at a near-equiatomic composition, a metastable ordered τ phase forms, which corresponds to a local minimum of the free energy. This phase can decompose to form equilibrium phases enriched in Al or Mn.

In experiments at a high temperature of $T = 973$ K and low treatment intensity, the τ phase remained stable; i.e., metastable equilibrium persisted, which corresponds to sector I of the diagram (Fig. 3). The higher-intensity treatment at the same temperature led to decomposition into equilibrium phases $\beta\text{-Mn} + \text{MnAl-r} (\gamma_2)$, which was likely induced by grain boundaries and by the emergence of high-stress nonequilibrium grain boundaries [55]. We observed a similar scenario at a lower temperature of 773 K. The change of the scenario of transformation corresponds to passage from sector I to sector II of the proposed diagram. Note that, in this system, there was no dynamic

recrystallization at $T = 773$ K; this fact favored the formation of segregations on grain boundaries.

In the treatment of the alloy in a ball mill at room temperature ($T = 300$ K), the τ phase remained stable in composition, which indicated that bulk diffusion under these conditions was frozen. At the same time, there was disordering of the τ phase, which was likely to be caused by the passage of partial dislocations through the bulk of the grains according to the previously proposed [9] concept (sector V of the diagram). Decreasing the temperature to $T = 77$ K at the same treatment intensity led to the amorphization of the alloy (sector IV of the diagram). The fact that there is no amorphization at $T = 300$ K is likely explained by the action of atomic or crystal order restoration mechanisms, which completely degenerate at $T = 77$ K. This experiment also showed that the temperature conditions of disordering and amorphization for the chosen system do not always coincide, contrary to published conclusions [8].

5. CONCLUSIONS

The proposed classification of the possible scenarios of nonequilibrium transformations and the emerging structural states under SPD is based on simple, but sufficiently general, notions of the competition of processes of energy accumulation and its dissipation via available routes of phase and structural relaxation (plastic deformation, grain structure refinement, amorphization, dynamic recrystallization, generation of nonequilibrium point defects, and others). This classification provides a unified approach to explaining a large set of experimental facts and predicting the mechanism of the development of phase or structural instability with varying temperature or intensity of treatment.

6. ACKNOWLEDGMENTS

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