Micromechanics of strength and plasticity in nanostructured materials

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Abstract A brief review of the research activity provided during the last three decades in the Laboratory of Mechanics of Nanomaterials and Theory of Defects at the Institute for Problems in Mechanical Engineering of Russian Academy of Sciences in the field of micromechanics of strength and plasticity in nanostructured materials is presented. It covers the works aimed at explanation and theoretical description of the following features in mechanical behavior of these materials: deviations from the classical Hall-Petch law, homo- and heterogeneous nucleation of dislocations, grain boundary sliding and mechanisms of its accommodation, rotational deformation, deformation twinning, deformation-induced grain growth and refinement, and interaction between deformation and fracture processes. Some most important and interesting results are discussed and compared with available data of experimental studies and computer simulations.

1 Introduction

The present paper represents a brief review of the research activity provided in the Laboratory of Mechanics of Nanomaterials and Theory of Defects, founded by Prof. I.A. Ovid'ko (1961-2017) in 1991 at the Institute for Problems in Mechanical Engineering of Russian Academy of Sciences (IPME RAS), in the field of micromechanics of strength and plasticity in nanostructured materials (NSMs) during the last three decades. This activity has concentrated at the development of theoretical models describing the physical mechanisms responsible for novel and often unpredictable phenomena in the mechanical behavior of such NSMs as nanocrystalline, ultrafine-grained and nanocomposite metals, alloys and ceramics. In particular, the

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explanation and description of deviations in the dependence of the yield stress on the grain size from the classical Hall-Petch law (including the inverse Hall-Petch dependence), homo- and heterogeneous nucleation of dislocations, transition from translational to rotational plasticity, codevelopment and competing of different mechanisms of plasticity (dislocation glide, grain-boundary sliding, Coble creep, triple-junction creep, grain rotation, etc.), deformation twinning, stress-coupled migration of grain boundaries (GBs), pore and crack nucleation, fracture and toughening mechanisms have been in the focus of the studies. Most of these models were reviewed in more detail in parallel with work, experimental and theoretical, of other authors in monographs [1–5], textbook [6] and reviews [7–34]. It is also worth noting that elaboration of the majority of these models was initiated and guided by Prof. I.A. Ovid'ko who made a great contribution in the field. We devote this review to his memory as well as to the 35 anniversary of IPME RAS.

2 Deviations from the classical Hall-Petch law

The classical Hall-Petch law relates the yield stress σ_y of a polycrystalline solid with its average grain size d as follows [35, 36]:

$$\sigma_y = \sigma_0 + K d^{-1/2}, \tag{1}$$

where σ_0 and K are the material dependent constants; σ_0 is the friction stress required for dislocation glide in the single-crystalline material and K is just a slope of the linear dependence $\sigma_y(d^{-1/2})$. The physical interpretation of Eq. (1) may be given from different viewpoints (see, e.g., the reviews [37–39]), however, this law was treated as rather universal one until the invention of nanocrystalline metals (NCMs). In 1989, Chokshi et al. [40] first observed the inverse dependence of σ_y on $d^{-1/2}$ in nanocrystalline Cu, when σ_y decreased with grain refinement in the range from 16 to 8 nm and explained this effect by Coble creep that is mass transfer along GBs. A bit later, Jang and Koch [41] reported on direct dependence $\sigma_y(d^{-1/2})$ similar to (1) in nanocrystalline Fe in the range from 11 to 6 nm, which however could also be well described by the Kocks relationship $\sigma_y \sim d^{-1}$ [42]. These controversial data stimulated extensive experimental and theoretical research in the following three decades (see, e.g., [1–4, 7, 8, 11, 31, 39, 43–47] for review).

One of the first theoretical model of such kind was suggested by Gryaznov et al. [48] who extended the 'composite' model of Kocks [42] to the case of NCMs. They represented an NCM as a composite material in which the intragrain material was treated as single-crystalline matrix while the GBs as inclusions in the shape of oblate ellipsoids randomly spaced and oriented with volume fraction $c \approx 3\delta/d$, where δ is the GB thickness. Using the rule of mixture for the effective shear modulus of such a composite [49] and assuming linear relationships of the shear moduli of the composite components and their yield stresses satisfying Eq. (1) with corresponding constants for intragrain and GB phases, Gryaznov et al. [48] finally found the relationship

$$\sigma_y = \left(\sigma_{0m} + K_m\, d^{-1/2}\right)\,\left(1 - \frac{1-q^2}{2q}\,\frac{3\delta}{d}\right), \tag{2}$$

where σ_{0m} and K_m are the constants of the matrix and q is the dimensionless constant smaller than 1, which characterizes the effect of GB porosity on the GB constants: $q \approx \sigma_{0GB}/\sigma_{0m} \approx K_{GB}/K_m$ with σ_{0GB} and K_{GB} attributed to the GB phase. The lower is the atomic density of the interface, the smaller is the values of q. When Eq. (2) is plotted as a dependence $\sigma_y(d^{-1/2})$, the straight line in the usual Hall-Petch law will remain straight only at large d or else as $q \to 1$. For $q < 1$, its slope will gradually decrease with decreasing d down to some critical size d_c, where the effective Hall-Petch factor will change sign. The critical size d_c is easily found from the condition $\partial\sigma_y/\partial(d^{-1/2}) = 0$. Gryaznov et al. [48] showed that it may be estimated as $d_c \approx 9\delta\,(1-q^2)/(2q)$ in practically any nanocrystalline metal. They also demonstrated that the contradictions arising on comparison of experimental results obtained by Chokshi et al. [40] and Jang and Koch [41] can be resolved in the framework of this approach. It is worth noting that many similar models operating within the 'rule-of-mixture' approach have been later developed (see [3] for a review and references).

Another theoretical approach dealing with competition of different physical mechanisms of plasticity in intragrain and GB phases of NCMs, has been developed by many research groups. A great step ahead in this direction was done by Masumura et al. [50] who took into account the lognormal distribution of grain volumes in real NCMs. They assumed that, in larger nanograins, the plastic deformation is realized by the glide of lattice dislocations, which should lead to the classical Hall-Petch relationship (1), while in smaller grains, the Coble creep dominates, which results in the inverse Hall-Petch relationship like $\sigma_y \sim d^3$. As a result, the mean yield stress $\langle\sigma_y\rangle$, averaged over the sample volume, followed the classical Hall-Petch law, $\langle\sigma_y\rangle \sim \bar{d}^{-1/2}$, in the range of large average grain size ($\bar{d} > d^*$) and the inverse Hall-Petch law, $\langle\sigma_y\rangle \sim \bar{d}^3$, in the range of small average grain size ($\bar{d} < d^*$), where d^* is a grain size at which the classical Hall-Petch mechanism switches to the Coble creep mechanism [50].

In developing this approach, Gutkin et al. [51] suggested to replace the Coble creep mechanism by the GB sliding mechanism for NCMs produced by severe plastic deformation (SPD). In such NCMs, GBs are commonly in a non-equilibrium state due to some excess of extrinsic GB dislocations (GBDs) stored at the fabrication stage [52]. Some of these GBDs are capable to glide within GBs, thus providing the GB sliding [53, 54]. In this case, triple junctions of GBs serve as natural obstacles for the motion of gliding GBDs, and the critical stress, which is needed for the transfer of the GB sliding from one GB to other GBs in their triple junctions, can be treated as the yield stress for the NCMs produced by SPD. In the simplest model case, the yield stress is [51] $\sigma_y = p + q\,(l/d) + s\,(l/d)^2$, where p (> 0), q ($>$ or < 0) and s (> 0) are the material and structure dependent parameters of the model, and l is about of interatomic distance. By using the averaging procedure similar to that by Masumura et al. [50], Gutkin et al. [51] obtained significant deviation of the $\langle \sigma_y \rangle$ ($\bar{d}^{-1/2}$) dependence from the classical Hall-Petch law (1). The Hall-Petch slope started to decrease for $\bar{d}$ smaller than roughly 25 nm, in good accordance with experimental data obtained on as milled nanocrystalline NiAl powders [55]. However, this model gives no inverse Hall-Petch dependence. Interestingly, the measurements on heat treated nanocrystalline NiAl powders [55], in which the GB sliding had to be suppressed due to elimination of the excess density of extrinsic GBDs, did show the inverse Hall-Petch dependence. Gutkin et al. [51] showed that it could be well described by the model of Masumura et al. [50] with account for the Coble creep contribution.

Fedorov et al. [56] extended the approach of Masumura et al. [50] by including the contribution of mass transfer along triple junctions of GBs. As with GB diffusion, triple junction diffusion is capable of playing a very important role in plastically deformed NCMs, where the volume fraction of triple junctions of GBs is extremely high. It was shown that the competition between conventional lattice dislocation glide, grain boundary diffusional creep and triple junction diffusional creep, which is characterized by the $\sigma_y \sim d^4$ dependence, may results in the inverse Hall-Petch dependence for the yield stress of NCMs with finest nanograins [56]. In the exemplary case of nanocrystalline Cu, this was expected for $\bar{d} < d^* \approx 18$ nm, in good accordance with experiments of Chokshi et al. [40].

Recently, the problem of the inverse Hall-Petch dependence interpretation has appeared for nanocrystalline ceramics (NCCs) as well [31]. As before for nanocrystalline metals, some authors have reported on their observations of the inverse Hall-Petch dependence in NCCs, while some others have not. To resolve the contradictions, Sheinerman et al. [57,58] suggested two models describing the initial stage of plastic deformation in nanocrystalline ceramics. Within the first model, plastic deformation is realized via the thermally activated GB sliding, but without GB diffusion. Within the second model, plastic deformation occurs through the emission of lattice and GB dislocations from GBs and their triple junctions. Both models predict the transition from the direct to the inverse Hall-Petch dependence at some critical grain size. At the same time, the critical grain size for this transition can be smaller than the smallest grain size of the ceramic specimens fabricated in experiments. This explains the absence of the transition from the direct to the inverse Hall-Petch dependence in some experiments.

3 Homo- and heterogeneous nucleation of dislocations in NCMs

The origin of lattice dislocations, which are carriers of plastic deformation in the internal regions of nanograins, is one of the most disputable questions in NCMs. The problem is that such well- known sources of dislocations as the Frank-Read sources and the double-cross slip, which are responsible for dislocation nucleation and multiplication in conventional coarse-grained polycrystalline materials [59], are suppressed due to lack of space inside nanograins. On the other hand, many authors reported on experimental evidence of lattice dislocations, both perfect [60, 61] and partial [62–64], in NCMs. In the special case of shock-loaded nanocrystalline Ni, the density of observed dislocations was extremely high, $\sim 10^{16}$ m^{-2} [65]. Molecular-dynamics computer simulations demonstrated the generation of partial and extended perfect dislocations by GBs and their triple junctions [66, 67].

In our lab, two types of theoretical models for dislocation generation in NCMs were elaborated. The models of the first type describe the homogeneous nucleation of glide dislocation loops, while those of the second type deal with heterogeneous nucleation of various dislocation configurations at GBs. The classical theory of dislocations predicts that lattice dislocations can nucleate homogeneously under an extremely high shear stress of the order of the theoretical shear strength of the material [59]. Analyzing the high-resolution transmission electronic microscopy (HRTEM) images of crystalline lattice in deformed multicomponent titanium alloys called Gum Metals, Gutkin et al. [68] noticed some characteristic nanoscale lattice disturbances which could be considered as precursors of dipoles of edge dislocations. They called these precursors 'nanodisturbances' and described them theoretically as finite-arm dislocation dipoles with variable Burgers vectors. According to this model, the nanodisturbances form randomly under local stress and thermal fluctuations. They have at once finite (nanoscopic) sizes and very small (smaller than the interatomic distance in the material) Burgers vectors, which both can increase under shear stress. Eventually nanodisturbances can gradually transform first to the dipole of conventional partial dislocations and then to the dipole of perfect dislocations. It was shown, that this process requires much smaller stress level than the classical model of homogeneous nucleation of dislocations. Experimental evidence of direct transformation of nanodisturbances to dislocation dipoles and reverse transformation of the latters to nanodisturbances was demonstrated by Cui et al. [69] in their HRTEM *in situ* observations of Gum Metal deformation under tension.

The initial idea of homogeneous nucleation of dislocation dipoles from nanodisturbances [68] was later extended to generation of glide dislocation loops in NCMs [70–72] and used in modelling of twinning, GB sliding and fracture of NCMs [73–76].

Regarding the heterogeneous nucleation of dislocations in NCMs, a number of different models were suggested to describe the decay of low-angle tilt GBs into lattice edge dislocations [77–79], the emission of partial and perfect dislocations by GBDs [78, 80–84], GB disclinations [85–89], GB triple junctions [54, 80–82, 90, 91] and GB pores [92]. In particular, Bobylev et al. [77–79] showed that the decay of low-angle GBs into ensemble of mobile lattice dislocations in mechanically loaded NCMs causes local plastic deformation in the grain where the decay takes place, as well as in neighboring grains. The decay of one low-angle GB can initiate a chain decay of neighboring GBs and the generation of a shear band (a narrow region where plastic deformation is localized). The critical stress τ_c of GB decomposition characterizes the initial stage of plastic deformation occurring via the development of shear bands. For nanocrystalline Fe, the value of τ_c was estimated to vary from 0.5 GPa (for GB misorientation angle $\omega \sim 2°$) to 2.5 GPa (for $\omega \sim 10°$). Its average value $\langle \tau_c \rangle \sim 1.5$ GPa coincides with the experimentally measured value of the shear stress [93] at which shear bands are formed in nanocrystalline Fe.

Bobylev et al. [78] also proposed dislocation-based model describing emission of partial lattice dislocations from high-angle GBs nucleated on GBDs as well as experimentally observed effect of GB bowing. Through energetic description, both processes were found to be highly sensitive to applied mechanical stress and GB misorientation angle. The results of this theoretical model account for experimental observations of curved GBs [62] and emission of partial dislocations by GBs [62] in deformed NCMs.

Gutkin and Ovid'ko [80] considered the generation of rectangular lattice perfect, lattice partial and GB dislocation loops at similar pre-existent dislocation loops and showed that these modes of dislocation generation can effectively provide plastic flow transfer from grain to grain, from grain to GB, from GB to grain, and from GB to GB in deformed NCMs, depending on their geometric and material characteristics. Bobylev et al. [81, 82] further developed this approach and considered more general case of the generation of two (one after another) rectangular lattice partial dislocation loops at a pre-existent GB dislocation loop with these two new loops having arbitrary Burgers vectors making the gliding segments of the loops of either mixed (edge and screw) or screw types (before they were of the edge type only [80]). Three different dislocation slip systems typical for the face-centered cubic (FCC) crystalline lattice were considered and it was found that emission of the partial dislocation loops belonging to the 60°-I slip system is the most probable in nanocrystalline FCC metals. This model also allowed to establish that experimentally detected [64] anomalously wide stacking faults in nanocrystalline Al are caused by high stresses but not by small grain size as was initially believed [64, 94, 95].

In a similar manner, Bobylev et al. [96] considered the generation of lattice partial dislocations at amorphous GBs in NCCs. In contrast to conventional GBs that emit lattice dislocations due to transformations of pre-existing GBDs (see above), the micromechanism of emission from amorphous GBs is different. Within the framework of the model, a dipole of immobile non-crystallographic edge dislocations is generated at the triple junctions (at the ends of an amorphous GB) through local shear events in this GB. These dislocations can split resulting in emission of partial lattice dislocations into grain interior. It was concluded that this process is energetically favorable and can proceed in athermal way in nanocrystalline 3C–SiC. The critical stress required to carry out this process was found to decrease with an increase of the GB length (in fact, the grain size). In other words, the transition from intergranular slip to intragranular dislocation slip becomes more difficult as the grain size decreases.

Fedorov et al. [54] focused their attention on the emission of lattice dislocations from the head of a pile-up of GBDs pressed to a triple junction of GBs in a deformed NCM. They calculated the energy barriers, which lattice dislocations must overcome to be emitted, and concluded that this process of stress relaxation at the GBD pile-ups looks hardly realistic as compared with some other possibilities such as emission of GBDs along the adjacent GBs. It is worth noting that this model has recently been used as a component of more general models aimed at the explanation and theoretical description of the effects of hardening by annealing and subsequent deformation-induced softening in ultra-fine grained (UFG) Al produced by high-pressure torsion [97–99].

Gutkin et al. [90, 91] analyzed in detail the emission of lattice dislocations from sessile GBDs which formed at triple junctions of GBs in the course of GB sliding during (super)plastic deformation of NCMs. In particular, they showed [90] that, in NCMs with FCC crystalline structure (Al, Cu and Ni), partial Shockley dislocations can be emitted from dislocated triple junctions to accommodate the GB sliding. In a similar way, the process of emission of perfect dislocations from dislocated triple junctions under superplastic deformation of NCMs was examined in [91]. The processes of accumulation of sessile GBDs at triple junctions and their further transformation through the emission of lattice dislocations were considered as mechanisms playing important roles in strengthening and softening of NCMs under superplastic deformation [91, 100].

Ovid'ko and Sheinerman [92] considered the emission of lattice and GB dislocations from nanovoids in single-phase and composite NCMs. They demonstrated that a GB nanovoid that serves as a sink for dislocations and therefore contains a dislocation with a large Burgers vector can emit lattice dislocations at room temperature. In contrast, the emission of lattice dislocations or lattice dislocation dipoles from a dislocation-free nanovoid is not realistic at room temperature. At the same time, a dislocation-free nanovoid at a GB can emit individual GB dislocations or GB dislocation dipoles. This provides a mechanism for void growth via GB dislocation emission in deformed NCMs.

4 Grain boundary sliding and mechanisms of its accommodation

Among the modes of GB mediated plastic deformation, one of the key mechanisms is GB sliding. In particular, it has been experimentally proven that GB sliding processes dominate during superplastic deformation of NCMs and NCCs [1]. Computer simulations [101, 102] also confirm the key role of GB sliding in plastic deformation of NCMs, especially at high stresses and strain rates [103]. GB sliding is plastic shears localized within GBs and normally it creates defects — sources of internal stresses — in GB triple junctions [1, 104] capable of initiating the nucleation of nanocracks [1, 104] and subsequent brittle fracture of the nanomaterial [104]. However, in the material, in parallel with GB sliding, accommodation processes can develop, which transform defects produced by GB sliding severely reducing the level of internal stresses and increasing ductility and fracture toughness of the nanomaterial. Understanding the micromechanics of these accommodation processes provides key insight in the nature of superplastic deformation of NCMs and NCCs.

Typical GB sliding accommodation mechanisms include the emission of lattice dislocations from GB triple junctions [1, 54, 90, 91], diffusion [73, 105], and rotational deformation [106]. At the same time, some original approaches have been developed in our lab like accommodation via GB splitting and migration [107, 108].

In particular, Bobylev et al. [108] developed a theoretical model of the mechanism of cooperative action of GB sliding, GB splitting and GB migration, which plays the role of a special mode of plastic deformation in NCMs. It was shown that GB sliding and GB migration are able to effectively accommodate each other by transforming GB disclinations. It was shown theoretically (using nanocrystalline Ni as an example) that the ductility and fracture toughness of a material increases if the described cooperative mechanism dominates over pure GB sliding or cooperative GB sliding and migration (without GB splitting [107]). The results of theoretical analysis (in particular, the formation of nanograins in the vicinity of GB triple junctions) are consistent with experimental data [109, 110] and computer models [111, 112] on the observation of nano- and microscopic grain nucleation at triple junctions.

Accommodation of GB sliding affects not only ductility, but fracture toughness as well. Bobylev et al. [73] investigated fracture toughness enhancement by means of non-accommodated and accommodated GB sliding in NCMs at low and medium temperatures, respectively. In the case of non-accommodated GB sliding, immobile non-crystallographic Volterra dislocations are produced at GB triple junctions near crack tips at relatively low temperatures. For nanocrystalline Al, Ni, and 3C–SiC, using the force criterion of crack growth, it was calculated that the effective stress intensity factor K^*_{IC} (fracture toughness) increases by up to 30% due to the dislocation created by non-accomodated GB sliding. The effect is stronger when dislocation is closer to the triple junction. The sensitivity of the stress intensity factor to this distance correlates with the sensitivity to grain size, since the smaller the grain size, the greater the probability of detecting a triple junction near the crack tip. At higher temperatures, GB sliding is effectively accommodated by diffusion-controlled climb of GBDs and emission of lattice dislocations into the grain body. Accommodated GB sliding can lead to significant blunting of crack tips, which, in turn, significantly (from 1.1 to 3 times, depending on temperature) increases fracture toughness. This effect is most pronounced in nanomaterials with very small grain sizes and decreases significantly with increasing grain size as $K^*_{IC} \sim d^{-5/2}$.

Bobylev et al. [106] considered a special mechanism of transition from GB sliding into rotational deformation in NCMs. This transition is also a mechanism for the accommodation of GB sliding. The mechanism was effectively described through the formation of immobile wedge disclinations at GB triple junctions characterized by gradually increasing power. Calculations using Ni and α-Al_2O_3 as examples demonstrated that this mechanism is energetically favorable. Typical values of the equilibrium disclination power (which is equal to the angle of grain rotation) were found to be in the range from 3° to 7.5° in nanocrystalline Ni when applied shear stress $\tau = 0.5$ GPa, and from 4° to 11° in nanocrystalline α-Al_2O_3 when $\tau = 2$ GPa.

5 Rotational deformation in NCMs

It is well known that the unique deformation behavior of NCMs is treated to be caused by suppression of conventional lattice dislocation slip and effective action of alternative deformation mechanisms occurring through generation, transformation and motion of GB defects. One of such defects are disclinations which are considered as carriers of rotational plastic deformation in solids [113, 114]. Experimental evidence of wedge disclinations in NCMs was demonstrated by Murayama et al. [115].

In the 1990-s, the efforts of our lab were concentrated on theoretical description of transformation of wedge disclinations placed at GBs and their triple junctions as well as on crack generation in their vicinity. Gutkin and Ovid'ko [116] considered the splitting of a wedge triple-junction disclination of strength Ω into a circular periodic array of N similar disclinations of smaller strength Ω/N and related this process with solid-state amorphization of the triple junction. They showed that such a process can effectively compete with generation of microcracks at the GB triple junctions, thus making the material more ductile. Gutkin et al. [117–119] suggested similar models for linear splitting of GB disclinations.

In the early 2000-s, the motion of dipoles of disclinations in NCMs was in the focus of research. Ovid'ko [120] and Gutkin et al. [88] considered deformation mechanism occurring through the motion of GB disclination dipoles as the mechanism of rotational deformation effectively contributing to the plastic flow in NCMs. As was assumed, the rotational deformation realized only due to movement of the GB disclination dipoles along parallel GB facets, accompanied by crystal lattice rotation between these facets. Gutkin et al. [121] analyzed the mechanisms of generation of mobile disclination dipoles from various (dipole and multipole) disclination configurations at the kinks, double kinks and triple junctions of GBs and related these models with generation and propagation of misorientation bands in poly- and nanocrystalline metals under severe plastic deformation. Mikaelyan et al. [122] clarified some details of the disclination dipole motion through accepting edge dislocations from the surrounding material by means of computer simulations by combined discrete dislocation-disclination dynamics.

In fact, GBs in NCMs are short and curved, and different deformation mechanisms strongly influence each other. For example, according to experimental data [123], GB sliding and rotational deformation are the key mechanisms of superplastic deformation in NCMs. Gutkin et al. [124] suggested a theoretical model describing the combined action of GB sliding and rotational deformation in NCMs, with focuses placed on the crossover from GB sliding to rotation deformation occurring at triple junctions of GBs. In the model [124], grain rotations occurred via the splitting of gliding GBDs at triple junctions into climbing GBDs which moved along GBs adjacent to the triple junction and cause crystal lattice rotation in the grain interior. It was shown that the splitting of the GBDs effectively occurs at triple junctions with large values of the triple junction angle. The experimentally detected [123] grain rotations in superplastically deformed nano- and microcrystalline materials, where GB sliding is the dominant deformation mechanism, support the theoretical model [124].

Recently, Borodin et al. [125] developed a coupled model for grain rotation, dislocation plasticity and GB sliding in UFG solids and NCMs under high-strain-rate deformation. They showed that competition between primal rotation caused by dislocation activity and inverse rotation provided by diffusional flux leads to the appearance of a critical grain size below which grains maintain their initial form in the course of deformation process. Under quasi-static deformation conditions, they obtained the critical grain size of NCMs, which is equal to just a few nanometers that is close to the experimentally found value of 6 nm [126]; the other value, of about 200 nm, was obtained for UFG metals, which is also in a good agreement with microstructural investigations [127]. For larger grains, dislocation kinetics fully determines the angle of rotation and accommodation of GB sliding. Borodin et al. [125] also estimated the maximum strain rate, below which equiaxed grains are still possible during the deformation process. For NC and UFG copper, their model predicted the values of 50 s^{-1} and 6 s^{-1}, respectively, for this maximum strain rate.

6 Deformation twinning in UFG and NC materials

One of the main specific deformation mode, which greatly contributes to plastic flow in NC and UFG materials, is deformation twinning (DT). Following numerous experimental data, computer simulations and theoretical models [64, 83, 128–133], nanoscale DT effectively operates in NCMs with various chemical compositions and structures. In contrast to coarse-grained polycrystals, in which deformation twins are typically generated within grain interiors, in NCMs under mechanical load, twins are often generated at GBs; see [130] and references therein. In order to explain this experimentally documented fact indicative of specific deformation behavior of NCMs, it was suggested that nanoscale DT occurs through consequent emission of partial dislocations from GBs [64, 128–130]. According to this explanation scheme, partial dislocations should either pre-exist at GBs on every slip plane or be resulted from transformations of pre-existent GBDs located on every slip plane to form a single twin through dislocation emission from the GB. However, it is practically impossible to have pre-existent GBDs or partial ones at a GB on every slip plane in real materials [64]. In order to avoid the discussed discrepancy, Zhu et al. [64] suggested that multiplication of partial dislocations can occur through dislocation reactions and cross-slip processes in deformed nanomaterials. As a result of such defect transformations, partial dislocations are capable of existing at a GB on every slip plane, in which case their consequent emission events provide a twin to grow continuously [64]. However, within this explanation, each dislocation reaction transforms a partial dislocation into two dislocations: a perfect dislocation and another partial dislocation. As a corollary, the dislocation reactions in question are characterized by very large energy barriers being of the order of the perfect dislocation energy. Such reactions can come into play, if only a very high level of the applied stress acts in a specimen. Therefore, multiplication of partial dislocations is hardly typical in NCMs in wide ranges of their deformation parameters. This motivates search for new alternative explanations of twin generation at GBs in mechanically loaded NCMs.

Gutkin et al. [83] suggested a theoretical model of deformation twin formation from the region at a GB, which occurs in the local stress field created by a biaxial dipole of triple-junction wedge disclinations. Sequential emission of twinning

Shockley partial Shockley dislocations under the combined action of the disclination and external shear stresses were modeled and analyzed in detail. It was shown that, in the exemplary cases of NC aluminum and copper with the average grain size of 30 nm, if the applied stress τ and disclination strength ω are high enough (but still realistic for NCMs), the DT generation is characterized by the absence of any energy barrier and the critical stress τ_c causing the emission of the first twinning dislocation is rather low, ~0.1 GPa and ~0.3 GPa, for Cu and Al, respectively, at $\omega = 0.5$. The generation of a thick DT lamella needs some increase in τ_c. That is, DT in NCMs is characterized by local strain hardening. Similar results were obtained by Gutkin et al. [131] when considering generation of deformation twin near of the tip of a microcrack of mixed modes I and II in a sample of NCM under tension.

Within another approach described in theoretical works of Ovid'ko and Skiba [132, 133], nanoscale deformation twins are generated at locally distorted GBs that contain local, deformation-distorted fragments with GBDs located on every slip plane and produced by preceding deformation processes. The twinning mechanisms represent (i) the successive events of partial dislocation emission from GBs; (ii) the cooperative emission of partial dislocations from GBs; and (iii) the multiplane nanoscale shear generated at GBs. It was found that the deformation twinning mechanisms can operate in NC and UFG materials at rather high, but realistic levels of the stress. The suggested representations on generation of nanotwins at locally distorted GBs logically explains numerous experimental observations [64, 129] of generation of nanoscale twins at GBs in NC and UFG materials. These deformation twinning mechanisms illustrate complicated interactions between different deformation modes such as deformation twinning, GB sliding and GB dislocation climb.

7 Deformation-induced grain growth and refinement in UFG and NC materials

UFG and NC structures are typically formed due to severe plastic deformation that causes grain refinement in initially coarse-grained structures. In order to control the final UFG and NC structures in severely deformed materials, it is important to understand and describe both the nature and micromechanisms of deformation-induced grain refinement. In these circumstances, of particular interest is the stress-driven GB migration which by definition represents a plastic deformation mode carried by migrating GBs [134]. It is conventionally treated that the stress-driven GB migration is responsible for both nanoscale plastic flow and grain growth [134].

A brief summary of early experimental observations of athermal stress-driven grain growth and GB migration is given in [135]. Gutkin and Ovid'ko [136] suggested probably the first simple analytical model to describe this phenomenal. They treated the migration of a tilt GB, characterized be the length $2a$ and the misorientation angle ω, over a distance d under an applied shear stress τ as an athermal process accompanied with generation of a quadrupole of partial wedge disclinations with strength ω and sizes $d \times 2a$. Analyzing the energy change caused by this process, they found two critical stress values: τ_{c1} which is necessary for starting the GB migration, and τ_{c2} which separate the stable and unstable regimes of the GB migration. These critical stresses are given by very simple formulas [135, 136]:

$$\tau_{c1} \approx \frac{D\omega b}{2a}\left(\ln\frac{2a}{b}+\frac{1}{2}\right), \quad \tau_{c2} \approx 0.8D\omega, \tag{3}$$

where $D = G/[2\pi(1-\nu)]$, G is the shear modulus, ν is the Poisson ratio, and b is the interatomic distance. It was also shown that, if $\tau_{c1} \le \tau < \tau_{c2}$, the equilibrium distance d_{eq} of the GB migration is determined from the following equation:

$$\tau = \frac{D\omega\, d_{eq}}{2a}\ln\left(1+\frac{4a^2}{d_{eq}}\right). \tag{4}$$

If $\tau \ge \tau_{c2}$, the GB migration becomes unstable when the GB propagation does not depend on the value of τ. This model was later supported by computer simulations [137].

Gutkin et al. [135, 138] extended the model [136] to the case of cooperative migration of two neighboring GBs with opposite signs of misorientation angles. They showed that the elastic interaction of two migrating GBs leads to a decrease of the critical stress τ_{c1}. For GBs with misorientation angles of equal magnitude ω, the difference is $\Delta\tau_{c1} \approx 3D\omega b/4a$. In this case, the stress value τ_m, at which these GBs can meet, is given by $\tau_m \approx 1.6D\omega$. In general, it was shown that the stable migration of GBs at $\tau_{c1} \le \tau \le \tau_m$ leads to a decrease of the grain bounded by them at the cost of growth of the neighbor grains and can result in complete or partial annihilation of the GBs and the collapse of this grain. Unstable migration at $\tau > \tau_m$ can lead either to annihilation of GBs or to passage of them through each other, which can be considered as the disappearance of the grain and nucleation and growth of a new grain.

The models [135, 136, 138] described the GB migration in an infinite NCM. However, most of experiments on the stress-driven grain growth were done on thin films, either free standing or deposited on special substrates [134], in which case the role of free surface(s) could be important. To take this into account, Dynkin and Gutkin [139, 140] considered the migration of a tilt GB in a stretched ultrathin NC layer. In doing so, they suggested and analyzed two models. In the first model, the migrating GB emerges on the layer surface, while in the second it migrates in the bulk of the layer. It was shown that both the critical stresses, τ_{c1} and τ_{c2}, decrease with decreasing GB misorientation angle ω and layer thickness h, and with increasing GB length $2a$. While a GB migrates in the stable regime, its equilibrium displacement d_{eq} increases with increasing τ and $2a$, and with decreasing ω, and practically does not depend on h. Thus, the least resistant to the stress-induced growth must be larger grains having low-angle GBs which are placed near free surfaces in the thinnest layers. The most advantageous case for athermal grain growth is that in which the migrating GB emerges on the layer surface.

Alternative role of stress-driven GB migration as a process responsible for nucleation of new nano-grains in NC and UFG materials (stress-induced grain refinement) has been suggested and investigated in a number of works [108,109,141–146] within our lab. The common approach employed in these works is a disclination description of stress-induced GB splitting and migration (modeled as splitting and movement of disclination dipoles) resulting in nucleation of new nanograins. First models using this method were developed by Bobylev and Ovid'ko [141, 142]. Within the framework of these models, nanograin nucleation occurs through splitting and migration of GBs containing disclination dipoles produced by GB sliding and/or lattice slip. It was shown that the nanograin nucleation is energetically favorable in mechanically loaded NC Al and α-Al_2O_3 in certain ranges of their parameters and the external stress levels.

Models [141,142] considered simplified GB migration scenario producing rectangular nanograins. More realistic hexagonal grain shapes were considered by Bobylev et al. [108] in a similar manner. Further development of this approach included description [143] of nanograin nucleation near crack tips in NCMs, where GB splitting happened at a highly stressed, disclination-free region near a crack tip. The suggested theoretical models [108, 143] of plastic flow occurring through generation of nanograins at GBs in UFG materials were well consistent with the experimental observation [109] of nanograins generation at GBs in cobalt.

Morozov et al. [144] suggested a theoretical model which describes nanograin chain formation. In this model, the initial GB structure contained a quadrupole of disclinations located at GB junctions of a previously formed nanograin in a NC or UFG specimen. The final structure contained two neighboring nanograins which are elongated along the same direction and may serve as nuclei for experimentally observed [145] nanograin agglomerates (groups of nanograins with low-angle and/or special GBs within comparatively large grains having high-angle GBs) in NC and UFG materials.

Bobylev and Ovid'ko [146] extended description above on deformation-distorted GBs — non-equilibrium GBs containing trapped ensembles of lattice dislocations typical for NC and UFG materials produced by severe plastic deformation methods. It was concluded that the splitting processes in deformation-distorted GBs is specific to these GBs and do not have their analogs in the previously examined conventional, non-distorted GBs and lead to formation of new nanoscale (sub)-grains in nanomaterials. Thus, the stress-driven splitting of deformation-distorted GBs can effectively contribute to grain refinement in bulk metallic materials under severe plastic deformation.

Common feature of GB migration processes is the existence of unstable migration regime [108, 135–144, 146, 147] and corresponding critical stress τ_{c2} for its onset. When applied stress exceeds this critical stress, GB starts migrating uncontrollably until it is stopped at some obstacle or destroyed completely (which is the case with low-angle GBs). Bobylev and Ovid'ko [146, 147] assumed that this process is effectively controls grain refinement under SPD processing. It is known [148] that the grain size of metallic materials processed by SPD cannot be reduced below certain minimum value, i.e. there exists saturation of grain size. Indeed, grain refinement often occurs through formation and evolution of lattice dislocation cells [149]. In their turn, individual dislocations that form cell boundaries are generated at sources like Frank-Read ones. Thus, Bobylev and Ovid'ko [146,147] assumed that saturation of grain size in metals under SPD occurs when the dislocation cell boundaries start intensively migrating (in unstable regime) under stress and saturated grain size can be estimated via the balance of the critical stress τ_{c2} and the stress of Frank-Read source operation. The following estimation for saturated grain size d_s was obtained:

$$d_s \approx \frac{15\pi(1-\nu)b}{2\omega}. \tag{5}$$

Using Eq. (5) in the case of dislocation cell misorientation ~1°–3°, Bobylev and Ovid'ko [146, 147] estimated $d_s \sim 78 - 233$ nm in Cu and $\sim 80 - 239$ nm in Ni. These estimates are well consistent with experiments showing $d_s \sim 200$ nm in Cu processed by equal-channel angular pressing [150], and $d_s \sim 50 - 200$ nm in Ni processed by high pressure torsion [151, 152].

8 Interaction between deformation and fracture processes in NCMs

Another research topic of our lab concerned the theoretical studies of the interaction between plastic deformation processes and fracture in deformed NCMs. The first work in this field [153] considered the generation of nanocracks in the stress field of dislocations with large Burgers vectors formed in triple junctions of GBs due to the coalescence of GBDs. This model [153] assumes that both GB sliding and conventional lattice dislocation slip cause plastic flow of a NC specimen. This means that when a mechanical load is applied to the specimen, mobile GBDs (with the Burgers vectors parallel to GB planes) move, causing GB sliding. These dislocations stop at triple junctions of GBs, where GB planes are curved and thereby dislocation movement is hampered. At some critical shear stress, GBDs merge at a triple junction, producing a sessile triple junction dislocation. This process is an elementary act of plastic deformation involving GB sliding. The process under consideration repeats and is accompanied by an increase of the Burgers vector magnitude of the sessile dislocation at each step. Within the model [153], a nanocrack at the triple junction is generated to release the strain energy of the sessile triple junction dislocation. In this scenario, mobile GBDs that carry GB sliding also influence nanocrack generation.

The calculations [153] demonstrated that the triple junction nanocrack is characterized by the equilibrium length that corresponds to the stable, low-energy state of the nanocrack. The equilibrium nanocrack length is highly sensitive to the parameters characterizing the triple junction geometry, the specific energy of the nanocrack surface, and GBD storage at the triple junction. In particular, triple junction nanocracks nucleate and rapidly grow with rising the Burgers vectors of GBDs generated and accumulated at triple junctions due to GB sliding. More precisely, a stable nanocrack nucleates at a triple junction after just several (about 5) acts of the GBD coalescence at the triple junction.

The theoretical model suggested in [153] accounts for the experimental observation [154] of nanocracks nucleating at triple junctions during plastic deformation of nanocrystalline Ni samples exhibiting substantial ductility. Also, this model predicts a certain stability of triple junction nanocracks. This prediction is in agreement with experiments [154], in which good ductility of deformed NCMs and a non-catastrophic character of failure processes have been detected.

At the same time, at low strain rates and/or high enough temperatures, the process of dislocation accumulation at triple junctions and the resulting generation of nanocracks can be suppressed due to GB diffusion. GB diffusion can provide partial relaxation of the stress fields created by triple junction superdislocations and thereby hampers nanocrack generation at triple junctions. The theoretical study of the combined effect of GB sliding and GB diffusion [155] demonstrated that the intense generation of nanocracks occurs at some critical plastic strain, which depends on the strain rate and temperature. In particular, at high strain rate and low temperatures, when GB diffusion is low, the critical strain for the intense nanocrack generation is small. In contrast, at small strain rates and high enough temperatures, when GB diffusion is fast, the critical strain for nanocrack generation is large. In the latter case, during the extensive stage of (super)plastic deformation, the stress relaxation effect of GB diffusion is dominant, which causes suppression of nanocrack generation.

In addition to the formation of triple junction dislocations, GB sliding can also lead to the formation of another kind of defect – disclination dipoles [156]. The formation of disclination dipoles is related to the shift of triple junctions during GB sliding. If the formation of disclination dipoles is not accommodated by GB diffusion, the stress fields of these dipoles can result in strain hardening during plastic deformation of NCMs and, at the same time, can lead to the generation of nanocracks. The effects of such dislocation dipoles on strain hardening and nanocrack generation were theoretically analyzed in Refs. [156, 157]. It appeared that disclination dipoles can cause high strain hardening and, besides, lead to the formation of long enough nanocracks, whose equilibrium length can be comparable to the grain size. As a result, such nanocracks can merge, leading to the generation and growth of microcracks.

As in the case of triple junction dislocations, the stress fields of disclination dipoles produced due to GB sliding can be affected by GB diffusion. The study of the combined effects of GB sliding (accompanied by the formation of disclination dipoles) and GB diffusion [105] has demonstrated that the mechanical behavior of plastically deformed NC specimens depends on strain rate and deformation temperature. At high strain rates and/or low temperatures, NCMs fail due to enhanced cracking. At high temperatures and/or low strain rates, they fail due to necking. In contrast, at intermediate strain rates and temperatures, NCMs can demonstrate good ductility. The region in the parameter space (strain rate, temperature) where NC specimens do not fail due to cracking or necking shrinks with an increase in the plastic strain, and at some critical plastic strain, NCMs fail at any strain rate and temperature.

Beside initiating the formation of new cracks, GB sliding can also affect the growth of existing cracks (see Section 4, the discussion of work by Bobylev et al. [73]).

As is indicated above, in addition to triple junction dislocations, GB sliding can also lead to the formation of disclination dipoles, which can also affect the growth of the existing cracks. The effect of the GB-sliding-induced disclination dipoles on the growth of existing cracks was analyzed in Ref. [158]. It was demonstrated that GB-sliding-induced disclination dipoles can increase the critical length for the catastrophic crack growth and thereby toughen NCMs. The increase in the critical nanocrack length is especially pronounced at very small grain sizes of NCMs and high misorientation angles of their GBs.

In parallel with GB sliding, other plastic deformation mechanisms also influence the fracture processes in NCMs. One such mechanism is the stress-driven GB migration, which can result in the formation of a quadrupole of wedge disclinations [135]. The effect of GB migration on the generation of nanocracks and the growth of pre-existent cracks in NCMs has been examined in Refs. [159, 160]. It was shown that, similar to GB sliding, GB migration can promote the generation of nanocracks in the stress fields of disclination quadrupoles and, at the same time, hinders the growth of the pre-existent cracks, leading to a small increase of the fracture toughness (by 10–15%).

Another example of a plastic deformation mechanism specific to NCMs is rotational deformation, which is accompanied by the rotation of crystal planes in a specified grain [30]. Such rotational deformation can lead to the formation of a wedge disclination dipole [30]. The effect of rotational deformation on the fracture toughness of NCMs was theoretically analyzed in Ref. [161]. It was shown [161] that rotational deformation can increase the fracture toughness by 10–15%.

In many cases, various plastic deformation mechanisms can be combined and accommodate each other in NCMs. An example is GB sliding accommodated by GB migration. Such mechanism was first suggested in Ref. [107]. The study of the effect of such deformation mechanism on the fracture toughness of NCMs [162] showed that this mechanism can dramatically increase the fracture toughness of NCMs (by a factor of 3 or more).

The importance of the above toughening mechanisms acting in NCMs is related to the low fracture toughness documented in these materials, which is much smaller than that of their coarse-grained counterparts. To explain the low fracture toughness of NCMs, the authors of Refs. [163, 164] considered the emission of dislocations from a tip of a large crack. Within the models [163,164], the first emitted dislocation stops at a nearest GB. As a result, a pileup of dislocations is produced ahead of the crack tip, whose length decreases with a decrease in grain size. The emitted dislocations can increase the fracture toughness in two ways: first, due to their stress fields that shield the crack tip, and, second, due to crack blunting. In coarse-grained metallic materials, the number of emitted dislocations can be large, and both toughening effects are strong. Therefore, such materials have high fracture toughness. In contrast, in NCMs, the length of dislocation pileups between the crack tip and the nearest GB is small. As a result, the number of dislocations emitted from a crack tip is also small, and their toughening effect is not essential. This explains the low fracture toughness of NCMs.

9 Conclusions

Thus, we gave a brief review of research efforts provided in our lab over almost 30 years on the development of theoretical models describing various aspects of mechanical behavior of nanostructured materials. As one could see, our contribution to the field has been rather extensive. In fact, our models have covered many important areas in micromechanics of plasticity of these materials with touching, although rather rarely, some problems of their fracture. In conclusion, we should say that nanostructured materials are specific solids in which plastic deformation develops through simultaneous action of various interacting physical mechanisms involving all elements of the defect structure, both in the bulk of nanograins and in their boundaries and triple junctions. These structural elements continuously change in the course of plastic deformation that makes their theoretical modeling rather difficult but very interesting for sure.

At present, some new topics are in focus of research in our lab, which we have not touched in this review. They concern theoretical modeling in the following areas: (i) plastic deformation and fracture in metal-graphene nanocomposites, (ii) fracture toughness of ceramic-graphene nanocomposites, (iii) mechanical behavior of monolitic nanoceramics, and (iv) evolution of structure and mechanical properties in ultra-fine grained aluminum and aluminum-based alloys in the process of thermal and mechanical treatment. We hope that, in the future, we will be capable to present an extended review of results obtained in these fields as well.

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