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SUPERPLASTICITY AND DUCTILITY OF SUPERSTRONG NANOMATERIALS

I.A. Ovid'ko

Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vasil. Ostrov, St. Petersburg 199178, Russia

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Abstract. A short overview of key concepts on superplasticity and ductility of nanomaterials characterized by high strength is presented. We consider plastic and superplastic flow mechanisms operating in nanocrystalline materials and their sensitivity to grain size. Also, strategies to achieve good ductility in strong nanocrystalline and nanocomposite materials (highly desired for a wide range of applications) are discussed. The specific features of superplastic deformation in nanomaterials are analysed with focuses placed on underlying mechanisms of superplasticity and their interaction at the nanoscale level. Unresolved questions and future research directions in this rapidly growing area of nanoscience and nanotechnology are briefly discussed.

1. INTRODUCTION

New outstanding chemical, mechanical and physical properties are exhibited by nanocrystalline materials, solids composed of nanometre-scale grains (crystallites) (Fig. 1a). These properties represent the subject of multidisciplinary research efforts motivated by a wide range of their applications in high technologies. Of special importance from both fundamental and applied viewpoints are the outstanding mechanical properties of nanocrystalline materials often exhibiting the superstrength, superhardeness and enhanced tribological characteristics; see, e.g., reviews [1-5] and books [6,7]. At the same time, nanocrystalline materials commonly show low tensile ductility which essentially limits their practical utility. Recently, however, several examples of substantial ductility and even superplasticity – ability of a material to undergo large elongations (100% and more) without failure – of superstrong nanocrystalline materials have been reported [8-23]. Needless to say that nanocrystalline materials with unique combination of very high strength and superplasticity (or at least good ductility) represent ideal materials for a wide range of applications in aerospace and automotive industries, medicine, energy, sport products, etc. In order to develop these materials for high technologies and reach progress in the fundamental science of nanostructures, it is very important to understand the underlying mechanisms of the exciting phenomenon of superplasticity in the nanocrystalline matter. The main aim of this paper is to give a brief overview of key concepts (based on experimental

Corresponding author: I.A. Ovid'ko, e-mail: ovidko@def.ipme.ru

data and theoretical models) on plastic deformation mechanisms in nanocrystalline materials exhibiting ductility and superplasticity and to discuss unresolved questions and future directions in this hot research area.

2. PLASTIC DEFORMATION MECHANISMS IN COARSE-GRAINED POLYCRYSTALS, ULTRAFINE-GRAINED MATERIALS AND NANOCRYSTALLINE MATERIALS WITH INTERMEDIATE GRAINS

In general, the specific deformation behavior of nanocrystalline materials is related to their specific structural features. Nanocrystalline materials are solids composed of nanometre-scale grains divided by grain boundaries (Fig. 1a). Such grains are tentatively ball-like crystallites with characteristic sizes < 100 nanometres (nm), where 1 nm = 10^{-9} metre. Grain boundaries are plane or faceted (curved) layers (Fig. 1a) with thickness about 1 nm and atomic structure and properties different from those of grains [24]. Grain boundaries join at triple junctions (Fig. 1a) that are tube-like regions with diameter about 1-2 nm. Triple junctions are treated as line defects with structure and properties different from those of grains and grain boundaries [25]. With very small grains, the volume fraction occupied by both grain boundaries and their triple junctions is very high in nanocrystalline materials. It is contrasted to the situation with conventional coarse-grained polycrystals having large grains and a negligibly low volume fraction occupied by grain boundaries (Fig. 1b). The difference in the structure is responsible for the difference in the deformation behavior between nanocrystalline materials and coarse-grained polycrystals.

In particular, as it is well-known, the dominant deformation mechanism in conventional coarse-grained polycrystals is the lattice dislocation slip occurring in large grain interiors [26] (Fig. 1b). Its carriers are perfect lattice dislocations generated and stored in the form of dislocation cells/subgrains in grain interiors during plastic deformation. Grain boundaries serve as obstacles for movement of lattice dislocations. In doing so, grain boundaries influence the level of the yield stress, the stress at which plastic deformation starts to occur. It is described by the well-known classical Hall-Petch relationship between the yield stress $\boldsymbol{\sigma}$ and grain size d: $\sigma=\sigma_0 k d^{-1/2}$, where σ_0 and k are material param-

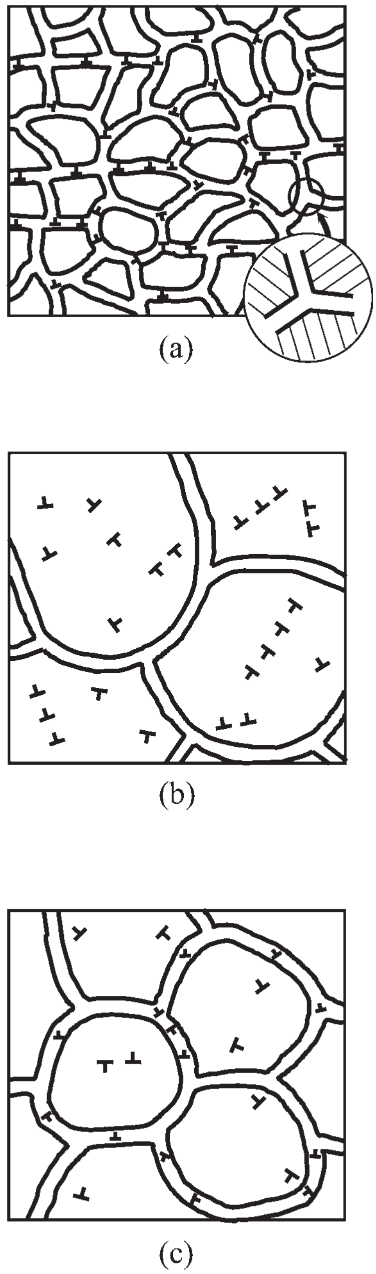

Fig. 1. Solid state structures under plastic deformation. (a) Nanomaterial with finest grains. (A large-scale view of a triple junction, its abuting grain boundaries and grains is shown in the low right corner of figure). Plastic deformation is conducted by grain boundaries. (b) Coarse-grained polycrystal. Lattice dislocation slip is dominant which gives rise to dislocation storage in large grain interiors. (c) Nanomaterial with intermediate grains. Lattice dislocation slip is dominant which is controlled by both dislocation storage and annihilation at grain boundaries.

eters [27,28]. However, in general, the mechanical behavior of coarse-grained polycrystals is crucially affected by evolution of lattice dislocations in grain interiors, but not grain boundaries. For instance, the deformation-induced storage of lattice dislocations in grain interiors in coarse-grained polycrystals is responsible for strenghening. It means that the flow stress increases with rising plastic strain. This standard deformation behavior is exhibited by most coarse-grained polycrystalline materials with grain size *d* being larger than 300 nm.

With grain refinement, the lattice dislocation slip shows deviations from the standard behavior due to both the nanoscale and interface effects. For illustration, let us consider materials with grain size *d* being in the range from tentatively 30 to 300 nm (Fig. 1c). This category of materials includes ultrafine-grained materials (*d* ranges from 100 to 300 nm) and nanocrystalline materials with intermediate grains (*d* ranges from tentatvely 30 to 100 nm). The lattice dislocation slip is still dominant in such materials. However, in contrast to the situation with conventional coarse-grained polycrystals, lattice dislocations are not intensively stored in grain interiors. In ultrafine-grained materials and nanocrystalline materials with intermediate grains, the level of the flow stress is crucially affected by grain boundaries operating as active sources and sinks of lattice dislocations [21]. More precisely, grain boundaries serve as the lattice dislocations sinks, in which case lattice dislocations are absorbed at grain boundaries and transformed into 'extrinsic' grain boundary dislocations. Also, grain boundaries serve as the lattice dislocation sources, in which case lattice dislocations are emited from grain boundaries, in particular, due to transformations of 'extrinsic' grain boundary dislocations. In these circumstances, both the storage and annihilation of dislocations at grain boundaries (but not in grain interiors) strongly influences the deformation behavior of ultrafine-grained materials and nanocrystalline materials with intermediate grains [21].

The dislocation storage and annihilation at grain boundaries are the two key competing factors crucially affecting the level of the flow stress. The dislocation storage at grain boundaries provides the strengthening of a material during plastic deformation. The dislocation annihilation at grain boundaries provides the softening (recovery) of a material during plastic deformation. Following [21], after some initial stage of deformation, the above competing factors reach equilibrium. That is, these factors cause a steady state in which the dislocation storage is completely compensated by the dislocation annihilation. The steady state is characterized by a tentatively constant flow stress without any strengthening. When the strengthening is absent, a material under tensile deformation commonly shows plastic flow localization in shear bands. Plastic flow localization in materials in the absence of the strengthening results in the macroscopic necking (Fig. 2a) followed by the stress concentration in the neck region. The local stresses acting in the neck region

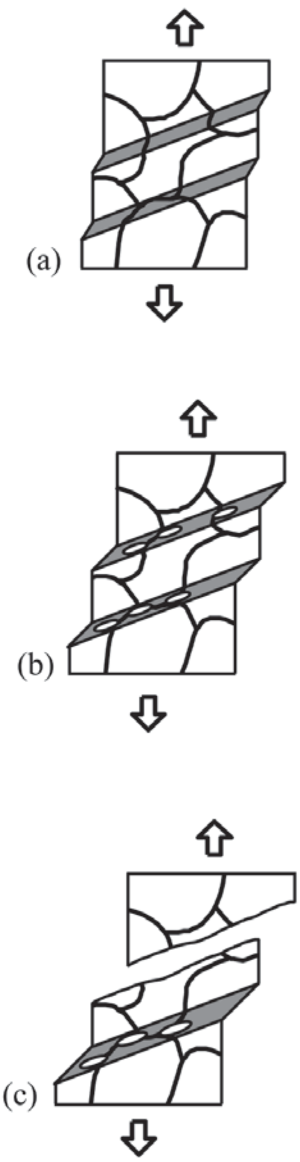

Fig. 2. Low tensile ductility of nanomaterials with intermediate grains. (a) Plastic flow localization in shear bands in nanomaterials with intemediate grains is followed by (b) nanocrack nucleation in shear bands and (c) macroscopic failure.

are very high; they become close to the critical stresses causing failure processes. In these circumstances, plastic flow localization (Fig. 2a) very quickly leads to intense crack (void) nucleation (Fig. 2b) followed by the macroscopic failure (Fig. 2c). As shown in a lot of experiments, this deformation behavior is typical for most ultrafine-grained materials and nanocrystalline materials with intermediate grains; see [21] and references therein.

3. PLASTIC DEFORMATION MECHANISMS IN NANOCRYSTALLINE MATERIALS WITH FINEST GRAINS

Now let us consider the specific deformation behavior of nanocrystalline materials with finest grains having grain size *d* lower than tentatively 30 nm (Fig. 1a). These materials under tensile deformation commonly show a brittle behavior with crack nucleation and propagation instability (Figs. 3a, 3b, and 3c), but without a preceeding neck formation. The brittle behavior is often due to fabrication-induced flaws serving as dangerous stress concentrators that cause the enhanced crack nucleation and propagation. With progress in fabrication technologies, it is currently possible to produce flaw-free nanocrystalline materials with finest grains. However, flaw-free nanocrystalline materials with finest grains also show ability to a brittle behavior due to their structural peculiarities. The volume fraction occupied by grain boundaries is extremely large in such materials. Therefore, the lattice dislocation slip is suppressed by high-density ensembles of grain boundaries, in which case alternative deformation mechanisms come into play in nanocrystalline materials with finest grains (Fig. 1a). These deformation mechanisms are conducted by grain boundaries and treated to be grain boundary sliding [29-31], grain boundary diffusional creep (Coble creep) [32,33], triple junction diffusional creep [34] and rotational deformation mode [35-39]; for a general view, see [1-7]. Also, recently, partial dislocation slip and twin deformation - deformation modes conducted by partial dislocations emitted from grain boundaries - have been experimentally observed in nanocrystalline materials [40-44].

Let us briefly discuss plastic deformation mehanisms conducted or stimulated by grain boundaries in nanocrystalline materials with finest grains. Grain boundary sliding means a relative shear of neighboring grains which is localized in the boundary between the grains (Fig. 4). Grain boundary sliding occurs through either movement of grain bound-

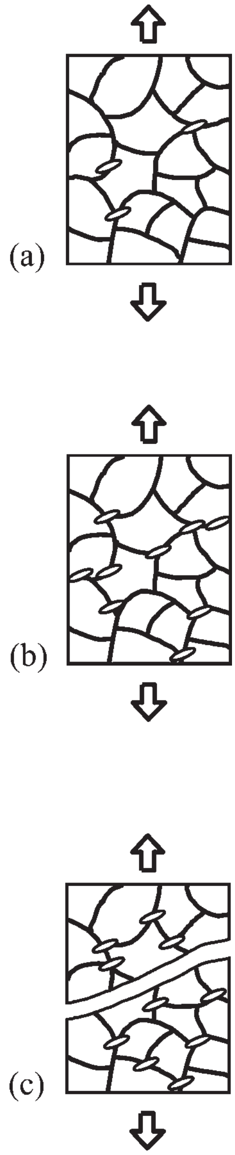

Fig. 3. Low tensile ductility of nanomaterials with finest grains. (a) Nanocrack nucleation in nanomaterials with finest grains is followed by (b) intense nucleation/convergence of new nanocracks and (c) macroscopic failure.

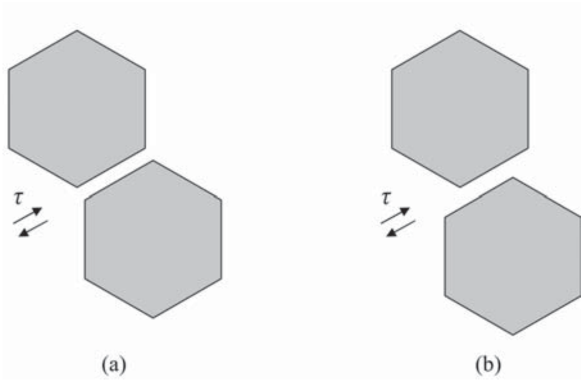

Fig. 4. Grain boundary sliding means a relative shear of neighboring grains (hexagons) which is localized in the boundary between the grains.

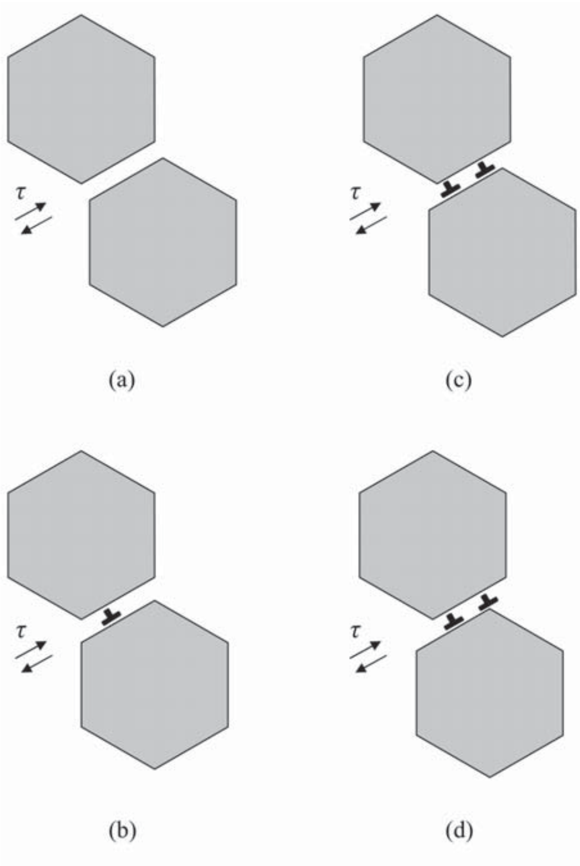

Fig. 5. Grain boundary sliding occurs through movement of grain boundary dislocations.

ary dislocations (Fig. 5) or local shear events in grain boundaries (Fig. 6). Local shear events or, in other words, atomic schufflng events in grain boundaries are shear transformations of elementary atomic clusters in grain boundaries. They are very similar to local shear events conducting viscous plastic flow in metallic glasses [45,46]. In terms of the dislocation theory, a local shear event is effectively treated as either nucleation of a dislocation loop [45] or formation of a kink pair at pre-existent line dislocaion. With this interpretation, for simplicity, in our following discussion, we will consider the mostly dislocation mode of grain boundary sliding.

Also, plastic deformation in nanomaterials with finest grains can occur through diffusional mass transfer. The diffusion coefficient along triple junctions sometimes is larger by several orders than the grain boundary diffusion coefficient [47] which, in its turn, is much larger than the bulk diffusion coefficient [24]. In these circumstances, enhanced diffusional mass transfer along grain boundaries and triple junction tubes is capable of essentially contributing to plastic flow in nanomaterials with finest grains especially at intermediate and high temperatures [32-34].

Rotational deformation in nanomaterials is conducted by grain boundary defects and gives rise to crystal lattice rotations in grains [35-39]. The rotational deformation can be effectively intiated by preceeding grain boundary sliding. In this case, a relative shear of two grains along their common boundary transforms into crystal lattice rotation in the third neighboring grain [38] (Fig. 7). (The relative shear of two grains along their common boundary is conducted by gliding grain boundary dislocations, whereas the crystal lattice rotation in the third neigh-

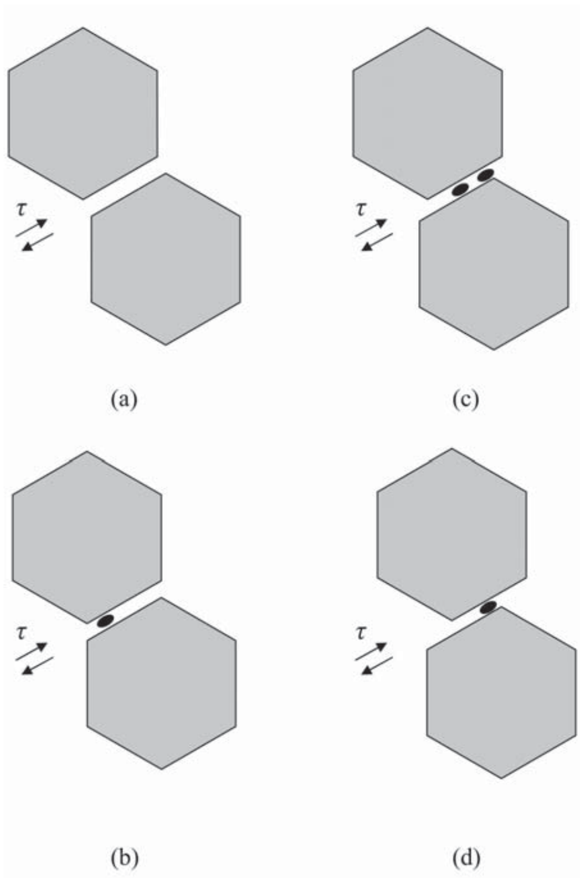

Fig. 6. Grain boundary sliding occurs through local shear events (ellipses) in grain boundaries. In terms of the dislocation theory, a local shear event is effectively treated as either nucleation of an isolated dislocation loop or formation of a kink pair at pre-existent line dislocation in the grain boundary phase.)

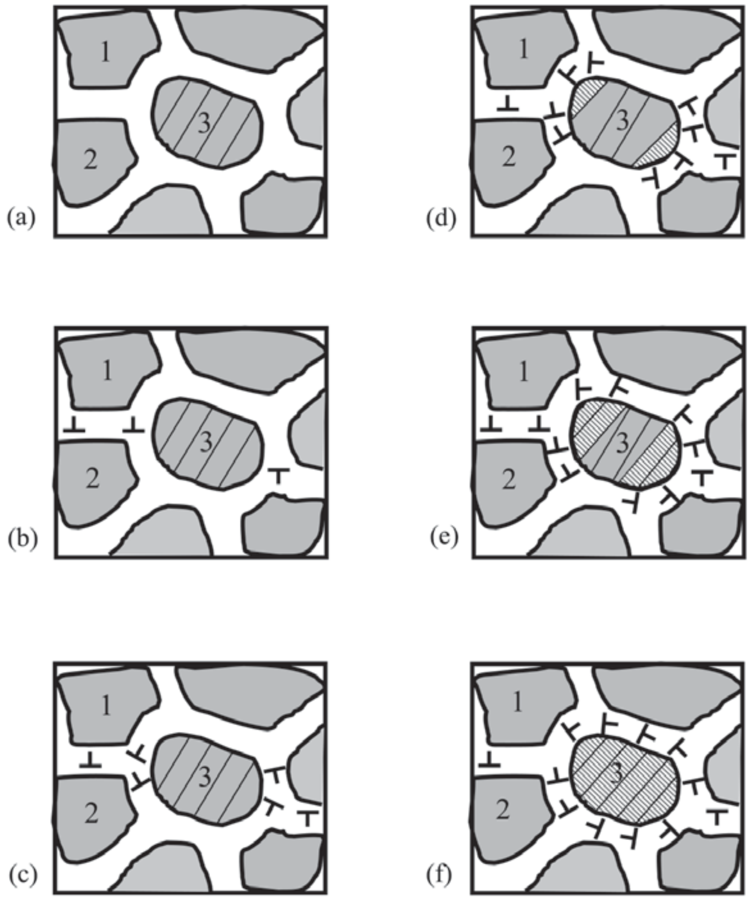

Fig. 7. Grain boundary sliding transforms into crystal lattice rotation in the neighboring grain in deformed nanomaterial. The relative shear of two nanoscale grains 1 and 2 along their common boundary is conducted by gliding grain boundary dislocations, whereas the crystal lattice rotation in the neighboring nanoscale grain 3 is conducted by climbing grain boundary dislocations.

boring grain is conducted by climbing grain boundary dislocations (Fig. 7).) Such crystal lattice rotations in grains have been experimentally observed in deformed nanomaterials showing ductility and superplasticity [35,36,39].

Partial dislocations that carry partial dislocation slip and twin deformation have been experimentally observed in nanocrystalline metals with finest grains [40-44]. In particular, pairs of partial dislocations emitted from grain boundaries and connected by wide stacking faults have been experimentally observed in nanocrystalline Al [44], wheras their formation in coarse-grained Al is commonly hampered due to high values of the specific stacking fault energy. These experiments are indicaive of the strong nanoscale and interface effects on the partial dislocation slip. Also, twin deformation has been experimentally observed in nanocrystalline metals like Cu and Al [40-44]. Twin deformation in nanomaterials can effectively occur through emission of groups of partial dislocations from grain boundaries and their further movement in grain interiors. Twin deformation plays an important role in nanomaterials deformed at low temperatures, in which case grain boundary sliding and grain boundary diffusion are suppressed.

Emission of partial dislocations from grain boundaries and associated twin deformation in nanomaterials can effectively occur as a result of transformations of 'intrinsic' and 'extrinsic' grain boundary dislocations in high-angle boundaries [48-50]. For instance, 'intrinsic' dislocations exist in equilibrium high-angle boundaries and carry, in part, misorientation between adjacent grains (for details, see [24]). The 'extrinsic' grain boundary dislocations are generated in high-angle boundaries due to transforma-

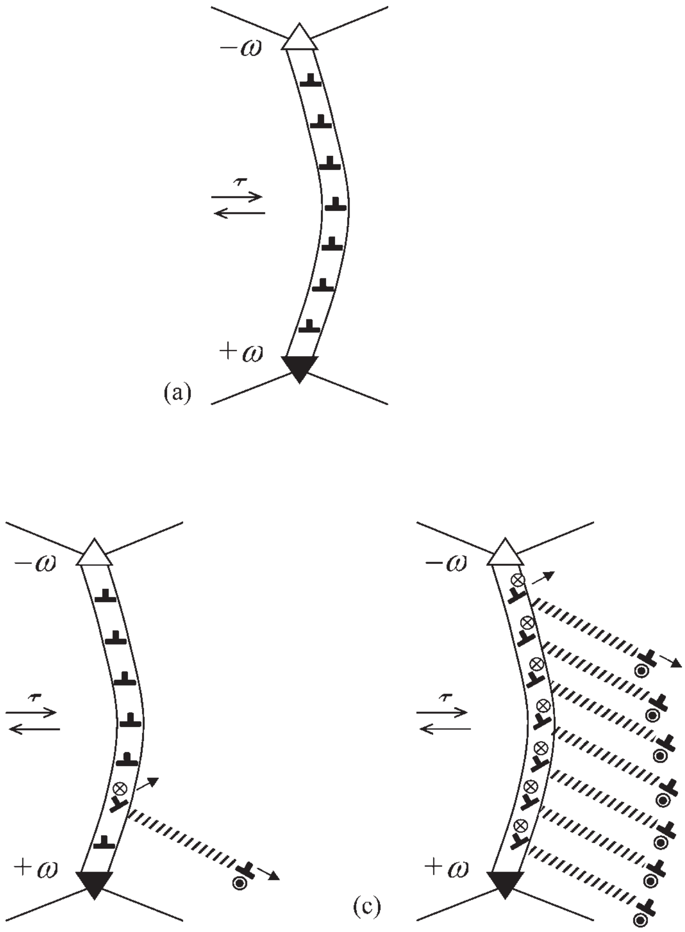

Fig. 8. Emission of partial dislocations from high-angle grain boundary. (a) High-angle grain boundary contains 'intrinsic' grain boundary dislocations and bows under the shear stress action. (b) Partial dislocation is emitted from grain boundary due to transformation (splitting) of a grain boundary dislocation. (c) Twin deformation occurs through emission of groups of partial dislocations from grain boundaries and their further movement in grain interiors. Twin occupies area swept by moving partial dislocations.

tions of lattice dislocations absorbed by grain boundaries; see. e.g., [2,5,6]. Both the 'intrinsic' and 'extrinsic' grain boundary dislocations under the shear stress action can undergo transformations resulting in emission of partial dislocations from high-angle boundaries; see, for instance, Figs. 8a and 8b. Twin deformation in nanomaterials can effectively occur through such transformations resulting in emission of groups of partial dislocations from grain boundaries and their further movement in grain interiors (Fig. 8 c).

Besides, lattice dislocations can be effectively emitted from grain boundary triple junctions due to storage of the unfinished plastic shear (in other terms, the Burgers vector) carried by either local shear events or grain boundary dislocations. For instance, local shear events (treated as events of dislocation loop nucleation [45] and driven by the shear stress action) intensively occur in a grain boundary whose plane is oriented along the maximum shear stress action (Fig. 9a). The boundary plane changes its orientation at the adjacent triple junction which thereby serves as obstacle for grain boundary sliding through local shear events. In these circumstances, the unfinished plastic shear or, in other terms, the Burgers vector is stored at the triple junction (Fig. 9b). When the stored Burgers vector magnitude reaches some critical value, a lattice dislocation of either prefect or partial type is emitted from the triple junction into a grain interior (Fig 9 c). The same scheme of the dislocation emission from grain boundary triple junctions, steps and facet junctions operates in the situation where grain boundary sliding is carried by grain boundary dislocations [51] (Figs. 9d, 9e, and 9f).

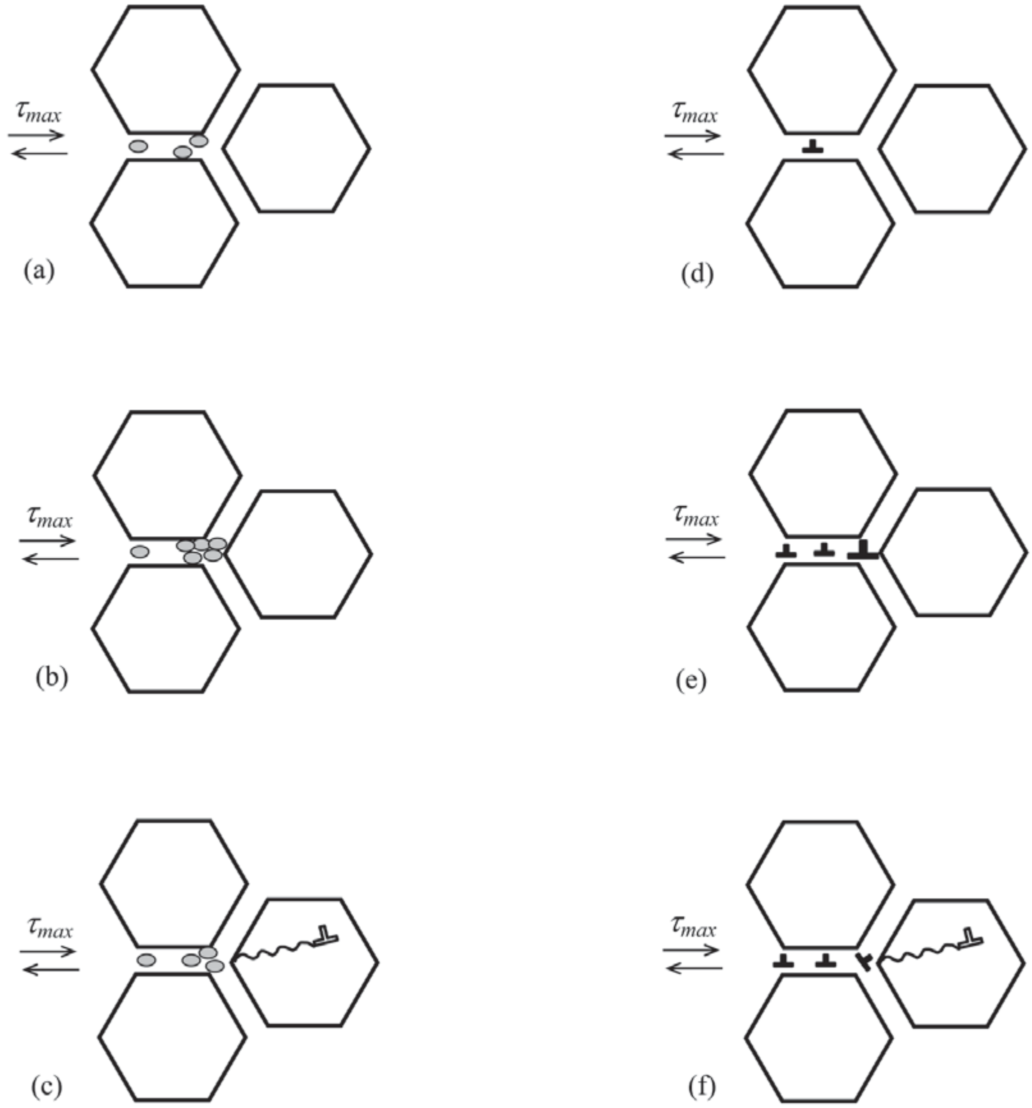

Fig. 9. Emission of partial dislocations from triple junction of grain boundaries. (a) Grain boundary sliding is realized through local shear events (events of nucleation of dislocation loops in grain boundary) driven by the shear stress action. Local shear events intensively occur in a grain boundary whose plane is oriented along the maximum shear stress action. The boundary plane changes its orientation at the adjacent triple junction which thereby serves as obstacle for grain boundary sliding through local shear events. (b) The unfinished plastic shear or, in other terms, the Burgers vector is stored at the triple junction due to local shear events. (c) When the stored Burgers vector magnitude reaches some critical value, a lattice dislocation of either prefect or partial type is emitted from the triple junction into a grain interior. (d) Grain boundary sliding is realized through movement of grain boundary dislocations which are stopped at triple junction. (e) The sum Burgers vector of grain boundary dislocations is stored at the triple junction. (f) When the stored Burgers vector magnitude reaches some critical value, a lattice dislocation of either prefect or partial type is emitted from the triple junction into a grain interior.

Thus, grain boundary sliding, grain boundary diffusional creep, triple junction diffusional creep, partial dislocation slip, rotational and twin deformation modes effectively operate in nanomaterials with finest grains. These deformation mechanisms are characterized by very high values of the flow stress which are much higher than those characterizing the lattice dislocation slip in conventional coarse-grained polycrystals and ultrafine-grained materials (Fig. 1c). At the same time, superstrong nanomaterials with

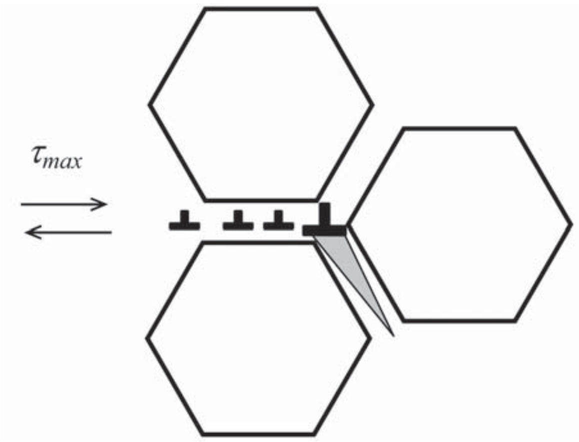

Fig. 10. Nanocrack generation occurs at dislocated triple junction in deformed nanomaterial.

finest grains commonly show low tensile ductility, in particular, due to the intense formation of nanocracks (Fig. 3). It is not surprizing, because superstrong solids are commonly brittle. Cracks are intensively generated at local stress concentrators, because high values of the flow stress are close to those needed to induce and sustain fracture processes.

For instance, the enhanced generation of nanocracks in deformed nanomaterials can occur at dislocated triple junctions [52,53] (Fig. 10) serving as dangerous stress concentrators in the situation where the lattice dislocation emission from the triple junctions and other accommodation mechanisms do not effectively operate. Such nanocracks in vicinities of triple junctions have been observed by Kumar with co-workers in 'in-situ' experiments with nanocrystalline Ni [20].

Thus, plastic deformation mediated by grain boundary processes in nanomaterials with finest grains is characterized by very high values of the flow stress and very quickly leads to intense nanocrack generation followed by macroscopic fracture (Fig. 3). Plastic deformation mediated by lattice dislocations in nanomaterials with intermediate grains is characterized by the absence of strengthening and very quickly leads to plastic flow localization followed by fracture (Fig. 2). The above factors, the absence of the strengthening in nanocrystalline materials with intermediate grains and very high flow stresses in nanocrystalline materials with finest grains, effectively explain numerous experimental data which are indicative of low tensile ductility exhibited by most nanocrystalline materials.

4. DUCTILITY OF NANOCRYSTALLINE AND NANOCOMPOSITE MATERIALS

Recently, several examples of substantial tensile ductility and even superplasticity of nanocrystalline materials have been reported [8-23]. With these experiments, the four basic strategies to achieve ductility in high-strength nanocrystalline materials with intermediate grains have been suggested; see, e.g., [8,17-19,54-58]. All these strategies are focused on suppression of plastic flow localization.

The first strategy is to suppress plastic flow localization through fabrication of a bimodal single-phase structure composed of nanograins and large grains (Fig. 11a). *The second strategy* is to suppress plastic flow localization through fabrication of a composite structure consisting of ductile second-phase inclusions embedded into a nanocrystalline matrix (Fig. 11b). These strategies are based on the large-scale structural organization of nanocrystalline materials and illustrated by the experimental facts that substantial ductility is exhibited by single-phase nanocrystalline materials with bimodal structure [4,8,19,21,54-56] and nanocomposites with a superstrong nanocrystalline matrix and ductile inclusions of the second phase [17,18,57]. Plastic flow localization is effectively hampered in such bimodal structures and nanocomposites due to the strengthening effects provided by large grains and inclusions of the second phase, respectively. For instance, large grains in bimodal structures (Fig. 11a) serve as rather ductile structural elements in which plastic deformation is characterized by strengthening. As a result, nanomaterials with the bimodal structure often have the same level of ductility as their coarse-grained counterparts and the same level of the flow stress as the yield stress of 'pure' nano-crystalline materials. Dendrite-like inclusions [17,18] of the second-phase cause similar effects in Ti-based nanocrystalline alloys which therefore show both essential ductility and high strength.

The third strategy is to deform nanocrystalline materials with intermediate grains at low temperatures [21,58]. In this case, recovery (the dislocation annihilation) processes at grain boundaries are suppressed and do not compensate the dislocation storage at such boundaries. As a result, a nanocrystalline sample under low temperature deformation often shows good ductility due to the strengthening that prevents plastic flow localization.

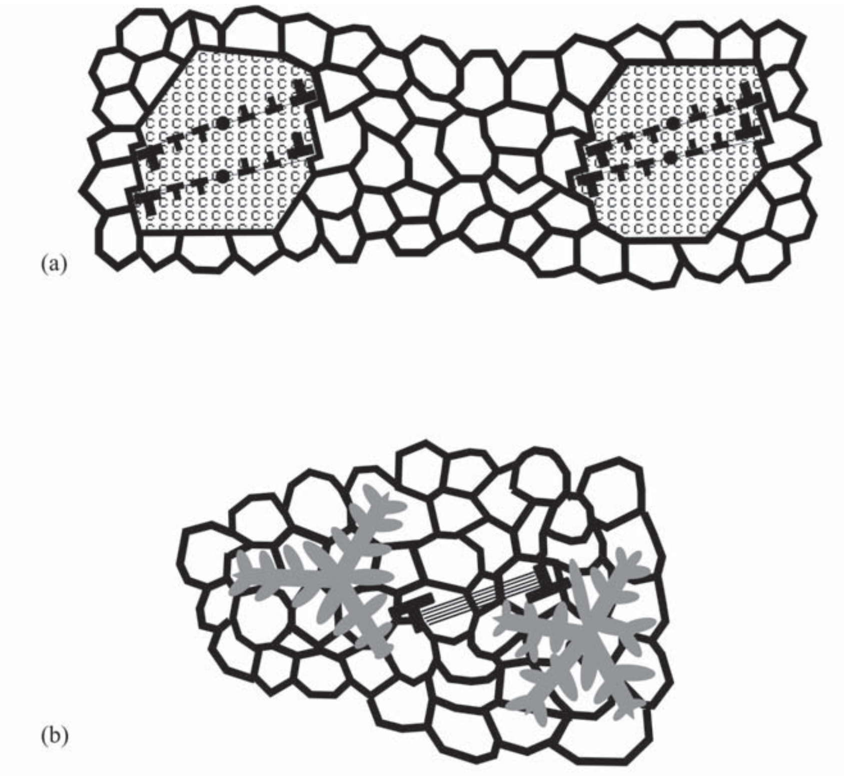

Fig. 11. Ductile nanomaterials with composite structure. (a) Single-phase nanocrystalline material with bimodal structure consisting of nanoscale and large (microscale) grains. (b) Nanocomposite consisting of nanoscale grains and dendrite-like inclusions of the second phase.

The fourth strategy is to suppress plastic flow localization through positive strain rate sensitivity of the flow stress τ. The sensitivity means that a local increase of the plastic strain rate in the neck region leads to a local increase of the flow stress τ. As a corollary, the neck formation is suppressed in nanocrystalline materials showing the positive strain rate sensitivity. This strategy, in part, is realized in superplastic deformation of nanocrystalline materials.

5. SUPERPLASTIC FLOW IN NANOCRYSTALLINE MATERIALS

Now let us discuss superplasticity in the nanocrystalline matter. In general, superplasticity denotes the ability of a solid to undergo large elongations (100% and more) without failure. Following experimental data [9-15], Ni, Ni_3Al, Al- and Ti-based nanocrystalline alloys (with the grain size being in the range from around 50 to 100 nm) show superplasticity at lower temperatures and higher strain rates compared to their coarse-grained counerparts. Superplasticity of nanocrystalline materials is characterized by very high values of the flow stress and the strengthening at the first extended stage of deformation; for a review, see [15]. At the same time, there is a rather extended second stage of superplastic deformation characterized by the softening.

In general, superplasticity occurs in superstrong nanocrystalline materials, if plastic strain localization and nanocrack nucleation/propagation instabilities are suppressed. In terms of plastic flow mechanisms, superplasticity can be reached due to the mechanisms providing the strengthening at the first stage of superplastic deformation, the positive strain rate sensitivity of the flow stress at the second stage and the absence of dangerous stress concentrators during both the stages of superplastic deformation.

Following experimental data [10-15], grain boundary sliding crucially contributes to superplastic flow in nanocrystalline materials. Also, lattice dislocation slip and grain rotations have been ex-

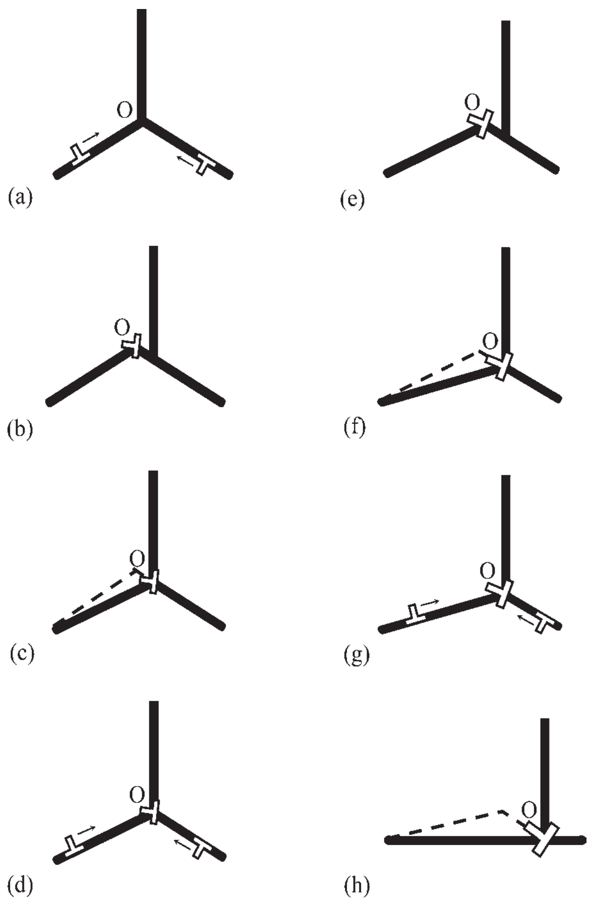

Fig. 12. Grain boundary sliding and transformations of defect structures near triple junctions of grain boundaries. (a) Initial state of defect configuration in a deformed nanocrystalline material. Two gliding grain boundary dislocations move towards the triple junction *O*. (b) Movement and convergence of two gliding dislocations results in the formation of sessile dislocation, plastic shear of upper grains relative to bottom grain and migration of the triple junction *O*. (c) Local grain boundary migration. (d) Movement of two new gliding grain boundary dislocations towards triple junction O. (e) Movement and convergence of two gliding dislocations results in an increase of Burgers vector magnitude of sessile dislocation, a plastic shear of upper grains relative to bottom grain and migration of the triple junction *O*. (f) Local grain boundary migration. (g) and (h) Grain boundary sliding via numerous acts of transfer of grain boundary dislocations across the triple junction *O* results in an increase of Burgers vector magnitude of sessile dislocation and the formation of a planar array of grain boundaries.

perimentally observed in nanocrystalline materials under superplastic deformation. With these experimental data and results of our theoretical models [5,6,31,38], we think that superplastic deformation occurs in nanocrystalline materials, if grain boundary sliding serves as the dominant deformation mechanism whose operation and effective accommodation are provided by lattice dislocation slip, intense diffuson, diffusion-controlled rotational deformation and triple junction migration.

As to details, grain boundary sliding is effectively supported by the lattice dislocatioin slip as follows. Lattice dislocations are effectively generated and move in intermediate grains of deformed nanocrystalline materials. (Following [26], the critical stress σ_c for activation of Frank-Read sources of lattice dislocations is given as $\sigma_c \sim Gb/ML$, where b denotes the magnitude of the lattice dislocation Burgers vector, M the orientation factor, G the shear modulus, and L the length of Frank-Read dislocation segment. In the case of nanocrystalline materials, L is around $d/3$, where d is the grain size [59]. For b = 0.3 nm, M = 0.5, and the grain size d range from 50 to 100 nm, we have $\tau_c \sim G/60 - G/30$. These values are close to experimentally measured [9-15] values of the superplastic flow stress in real nanocrystalline materials. Therefore, the flow stress level is high enough to activate Frank-Read sources of lattice dislocations in intermediate grains of nanocrystalline materials.) The lattice dislocations move towards grain boundaries where these dislocations are absorbed and transformed into grain boundary dislocations that carry grain boundary sliding. Mobile grain boundary dislocations – carriers of grain boundary sliding in nanocrystalline materials under superplastic deformation – glide along boundary planes [24] and come into dislocation reactions at triple junctions (Fig. 12). As a result of the dislocation reactions, sessile grain boundary dislocations are formed and stored at triple junctions (Fig. 12). The sessile grain boundary dislocations at triple junctions elastically interact with mobile grain boundary dislocations and thereby hamper their glide [5,6,31]. Thus, the storage of grain boundary dislocations (Fig. 12) causes the experimentally observed [8] strengthening of nanocrystalline materials at the first stage of superplastic deformation. It is contrasted to coarse-grained polycrystals where the strengthening is provided by the storage of lattice dislocations in grains [26].

The storage of grain boundary dislocations at triple junctions is capable of causing failure processes in deformed nanocrystalline materials, be-

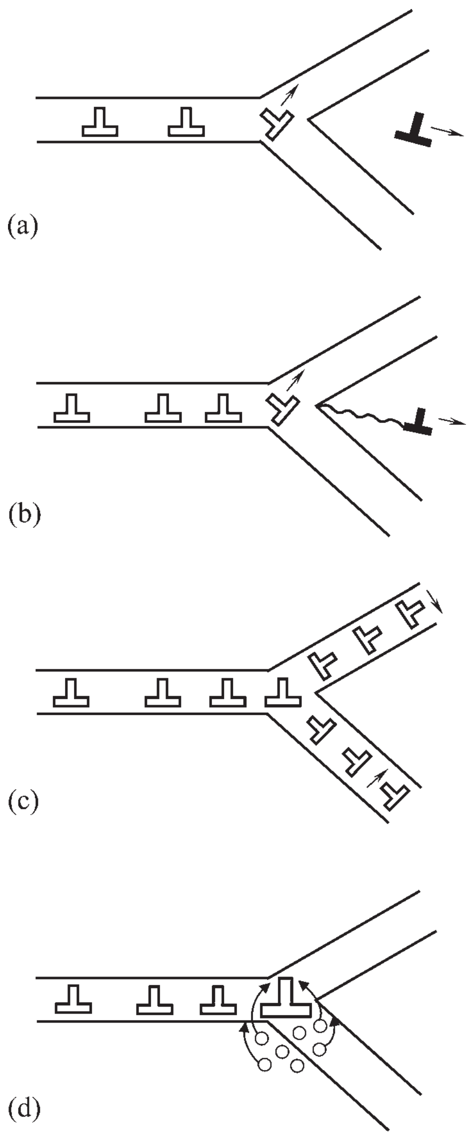

Fig. 13. Stress relaxation processes in deformed nanocrystalline materials. (a) Emission of perfect dislocation from triple junction. (b) Emission of partial dislocation from triple junction. (c) Crossover from grain boundary sliding to rotational deformation. Gliding grain boundary dislocations split into climbing grain boundary dislocations at triple junction. (d) Diffusional flows of vacancies provide a partial relaxation of stress fields of sessile dislocation at triple junction.

cause dislocated triple junctions serve as dangerous stress sources inducing the nucleation of nanocracks [52,53] (Fig. 10). Such nanocracks in vicinities of triple junctions have been observed by Kumar *et al.* in 'in-situ' experiments with nanocrystalline Ni [20]. Thus, the storage of grain boundary dislocations at triple junctions causes the two competing effects on tensile ductility and superplasticity of nanocrystalline materials. On the one hand, the dislocation storage provides the strenghening and thereby suppresses plastic flow localization. On the other hand, the grain boundary dislocation storage causes the formation of local stress concentrators and thereby enhances the nanocrack nucleation.

The suppression of the nanocrack nucleation in nanocrystalline materials under superplastic deformation can be reached due to the accommodation effects of the lattice dislocation slip [51, 60], diffusion-assisted rotational deformation mode [38] and local diffusion processes [61] (Fig. 13). In particular, emission of lattice dislocations from dislocated triple junctions (Figs. 9 and 13a and 13b) causes a decrease of the rate of the grain boundary dislocation storage at triple junctions and thereby suppresses the nanocrack nucleation. The rotational deformation effectively comes into play at triple junctions which stop grain boundary sliding. That is, the crossover from grain boundary sliding to the rotational deformation occurs at triple junctions whose geometry prevents further grain boundary sliding (Figs. 7 and 13c). In this case, the rotational deformation occurs through diffusion-assisted climb of grain boundary dislocations [38] (Figs. 7 and 13c) and serves as the key recovery process opposite to the grain-boundary-sliding-induced storage of grain boundary dislocations. This recovery process causes a decrease of the rate of the grain boundary dislocation storage at triple junctions and thereby suppresses the nanocrack nucleation. In addition, diffusional flows of point defects (Fig. 13d) provide a partial relaxation of the stresses of dislocated triple junctions and thereby hamper the nanocrack nucleation near these junctions [61].

The softening of nanocrystalline materials under superplastic deformation is related to triple junction migration that accommodates grain boundary sliding [30,31]. For instance, as shown in illustrative Fig. 12, grain boundary sliding - plastic shear of two upper grains relative to bottom grain along grain boundaries and triple junction – is accommodated by migration of triple junction and its adjacent grain boundary. More precisely, the triple junction migration gradually changes triple junction geometry (Fig. 12) and results in the experimentally observed [62] formation of tentatively plane arrays of grain boundaries (Fig. 12f). In doing so, triple junctions stop being obstacles for grain boundary sliding along coplanar grain boundaries. Therefore, cooperative grain

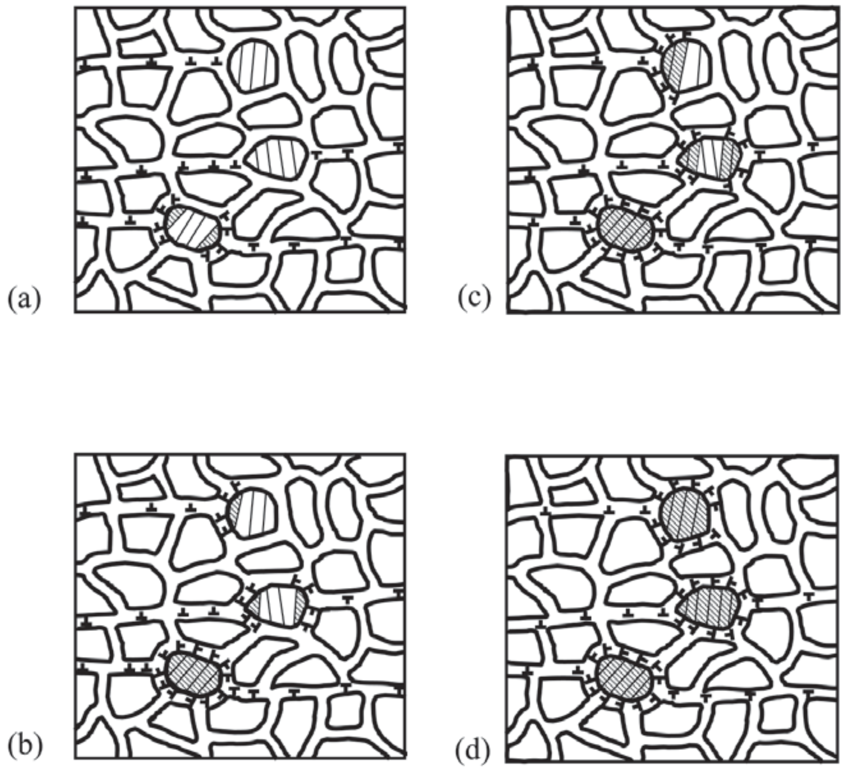

Fig. 14. Combined action of grain boundary sliding and rotational deformation mode in nanocrystalline material under superplastic deformation.

boundary sliding along co-planar grain boundaries is enhanced, and the strengthening at some critical plastic strain degree is replaced by the softening [31] that characterizes the second stage of superplastic deformation. At the second stage, enhanced cooperative grain boundary sliding occurs along plane arrays of grain boundaries. These arrays are commonly divided by grains whose geometry prevents grain boundary sliding (Fig. 14). In these grains, the enhanced grain boundary sliding transforms into a viscous-type deformation mechanism characterized by the positive strain rate sensitivity. A strong candidate is the slow rotational deformation mediated by diffusion-assisted climb of grain boundary dislocations (Fig. 14) and characterized by the positive strain rate sensitivity. In the situation discussed, both the enhanced grain boundary sliding and slow rotational deformation operate at the second stage of superplastic deformation (Fig. 14). The slow rotational deformation controls the plastic strain rate. With the positive plastic strain sensitivity of the rotational deformation, plastic flow localization is suppressed at the second stage of superplastic deformation.

Thus, superplastic deformation occurs in nanocrystalline materials, if grain boundary sliding serves as the dominant deformation mechanism whose operation and accommodation are provided by the lattice dislocation slip, intense diffusion, rotational deformation and triple junction migration.

6. CONCLUSIONS. UNRESOLVED QUESTIONS AND FUTURE RESEARCH DIRECTIONS

To summarize, owing to the specific structural features of nanocrystalline materials, the set of deformation mechanisms in these materials is richer than that in conventional coarse-grained polycrystals. In particular, grain-boundary-mediated deformation mechanisms – the rotational deformation, grain boundary diffusional creep, triple junction diffusional creep and grain boundary sliding – operate in nanocrystalline materials with finest grains (Fig. 1a). The deformation behavior of nanocrystalline materials with intermediate grains (Fig. 1c) is controlled by grain boundaries operating as active sources and sinks of lattice dislocations. Such materials show good ductility, if plastic flow localization is suppressed. Ni, Ni_3Al, Al- and Ti-based nanocrystalline alloys with intermediate grains show superplastic deformation characterized by very high values of the flow stress and the strengthening at the first extended stage [9-15].

Achievment of superplasticity or good ductility in superstrong nanocrystalline materials in a wide range of their compositions and realization of superplastic deformation in nanocrystalline materials at commercially desired high strain rates and room temperature are very important unresolved questions in this hot research area. In the context discussed, a theoretical description and experimental identification of superplastic flow mechanisms in nanocrystalline materials as well as determination of their structural characteristics and fabrication parameters that control/optimize superplasticity represent the future critical directions of research.

With available experimental data and theoretical models concerning superplastic flow mechanisms, we suggest that superplastic deformation occurs in nanocrystalline materials, if grain boundary sliding serves as the dominant deformation mechanism whose operation and accommodation are provided by the lattice dislocation slip, intense diffusion, rotational deformation and triple junction migration.

In this context, the following specific structural features of nanocrystalline materials can enhance their superplasticity:

(i) Nanocrystalline materials should contain high-angle grain boundaries being in their highly defective, non-equilibrium state. High-density ensembles of grain boundary dislocations at such grain boundaries carry grain boundary sliding and rotational deformation. High-density ensembles of point defects at non-equilibrium grain boundaries carry intense diffusion processes.

(ii) Nanocrystalline materials should not contain many low-angle boundaries that do not provide both grain boundary sliding and enhanced diffusion processes.

(iii) Nanocrystalline materials should have intermediate grains where Frank-Read sources of lattice dislocations effectively operate. In this case, lattice dislocation slip effectively supports grain boundary sliding and rotational deformation processes.

(iv) Nanocrystalline materials should contain mobile triple junctions whose migration and structural transformations provide respectively grain boundary sliding accommodation and transitions between grain boundary sliding, lattice dislocation slip and rotational deformation.

These statements are worth being taken into account in further experimental and theoretical studies of superplasticity of superstrong nanomaterials.

Finally, notice that geometry of grain boundary sliding at the nanoscale level is very similar to geometry of relative movement of Earth tectonic plates at the level of thousand kilometers. With this similarity, accumulation of sessile dislocations at triple junctions and its relaxation through the nanocrack nucleation in superplastically deformed nanocrystalline materials [20,48] (Fig. 10) serve as analogs of Earth stress accumulation at curved boundaries between tectonic plates and its relaxation through Earth quakes, respectively. In this context, nanocrack nucleation in deformed nanocrystalline materials represents a nanoscale model process for Earth quakes.

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REFERENCES

[1] K.S. Kumar, S. Suresh and H. Swygenhoven // *Acta Mater.* **51** (2003) 5743.

[2] R.Z. Valiev // *Nature: Mater.* **3** (2004) 511.

[3] D. Wolf, V.Yamakov, S.R. Phillpot, A.K. Mukherjee and H. Gleiter // *Acta Mater.* **53** (2005) 1.

[4] B.Q. Han, E. Lavernia and F.A. Mohamed // *Rev. Adv. Mater. Sci.* **9** (2005) 1.

[5] I.A. Ovid'ko // *Int.Mater.Rev.* **50** (2005) 65.

[6] M.Yu. Gutkin and I.A.Ovid'ko, *Plastic Deformation in Nanocrystalline Materials* (Springer, Berlin, Heidelberg, New York, 2004).

[7] *Mechanical Properties of Nanocrystalline Materials and Nanocomposites*, ed. by I.A. Ovid'ko, C.S. Pande, R. Krishnamoorti, E.J. Lavernia and G. Skandan (MRS, Warrendale, 2004).

[8] Y. Wang, M. Chen, F. Zhou and E. Ma // *Nature* **419** (2002) 912.

[9] S.X. McFadden, R.S. Mishra, R.Z. Valiev, A.P. Zhilyaev and A.K. Mukherjee // *Nature* **398** (1999) 684.

[10] R.K. Islamgaliev, R.Z. Valiev, R.S. Mishra, A.K. Mukherjee // *Mater. Sci. Eng.A* **304-306** (2001) 206.

[11] R.Z. Valiev, I.V. Alexandrov, Y.T. Zhu and T.C. Lowe // *J. Mater. Res* **17** (2002) 5.

[12] R.S. Mishra, V.V. Stolyarov, C. Echer, R.Z. Valiev and A.K. Mukherjee // *Mater. Sci. Eng. A* **298** (2001) 44.

[13] R.Z. Valiev, C. Song, S.X. McFadden, A.K. Mukherjee and R.S. Mishra // *Phil. Mag. A* **81** (2001) 25.

[14] R.S. Mishra, R.Z. Valiev, S.X. McFadden, R.K. Islamgaliev and A.K. Mukherjee // *Phil. Mag. A* **81** (2001) 37.

[15] A.K. Mukherjee // *Mater. Sci. Eng. A* **322** (2002) 1.

[16] Y. Champion, C. Langlois, S. Guerin-Mailly, P. Langlois, J.-L. Bonnentien and M. Hytch // *Science* **300** (2003) 310.

[17] G. He, J. Eckert, W. Loeser and L. Schultz // *Nature Mat.* **2** (2003) 33.

[18] G. He, M. Hagiwara, J. Eckert and W. Loeser // *Phil.Mag.Lett.* **84** (2004) 365.

[19] V.L. Tellkamp, A. Melmed and E.J. Lavernia // *Metall.Mater.Trans.* A **32** (2001) 2335.

[20] K.S. Kumar, S. Suresh, M.F. Chisholm, J.A. Horton and P. Wang // *Acta Mater.* **51** (2003) 387.

[21] Y.M. Wang and E. Ma // *Acta Mater.* **52** (2004) 1699.

[22] Y.T. Zhu and X. Liao // *Nature: Mater.* **3** (2004) 351.

[23] K.M. Youssef, R.O. Scattergood, K.L. Murty and C.C. Koch // *Appl.Phys.Lett.* **85** (2004) 929.

[24] A.P. Sutton and R.W. Balluffi, *Grain Boundaries in Crystalline Materials* (Oxford Sci., Oxford, 1996).

[25] A.H. King // *Interf. Sci.* **7** (1999) 251.

[26] J.P. Hirth and J.Lothe, *Theory of Dislocations* (Mc Graw-Hill, NewYork, 1968).

[27] E.O. Hall // *Proc. Phys. Soc. London B* **64** (1951) 747.

[28] N.J. Petch // *J. Iron Steel Inst*. **174** (1953) 25.

[29] D.A. Konstantinidis and E.C. Aifantis // *Nanostruct. Mater*. **10** (1998) 1111.

[30] K.A. Padmanabhan and H. Gleiter // *Mater. Sci. Eng.*A **381** (2004) 28.

[31] M.Yu. Gutkin, I.A. Ovid'ko and N.V. Skiba // *Acta Mater*. **52** (2004) 1711.

[32] R.A. Masumura, P.M. Hazzledine and C.S. Pande // *Acta Mater*. **46** (1998) 4527.

[33] H.S. Kim, Y. Estrin and M.B. Bush // *Acta Mater*. **48** (2000) 493.

[34] A.A. Fedorov, M.Yu. Gutkin and I.A. Ovid'ko // *Scr. Mater*. **47** (2002) 51.

[35] M. Ke, W.W. Milligan, S.A. Hackney, J.E. Carsley and E.C. Aifantis // *Nanostruct. Mater.* **5** (1995) 689.

[36] M. Murayama, J.M. Howe, H. Hidaka and S. Takaki // *Science*, **295** (2002) 2433.

[37] I.A. Ovid'ko // *Science* **295** (2002) 2386.

[38] M.Yu. Gutkin, I.A. Ovid'ko and N.V. Skiba // *Acta Mater*. **51** (2003) 4059.

[39] Z. Shan, E.A. Stach, J.M.K. Wiezorek, J.A. Knapp, D.M. Follstaedt and S.X. Mao // *Science* **305** (2004) 654.

[40] J.H. He and E.J. Lavernia // *J. Mater. Res.* **16** (2001) 2724.

[41] X.Z. Liao, F. Zhou, E.J. Lavernia, S.G. Srinivasan, M.I. Baskes, D.W. He and Y.T. Zhu // *Appl. Phys. Lett.* **83** (2003) 632.

[42] M.W. Chen, E. Ma, K.J. Hemker, H.W. Sheng, Y.M. Wang and X.M. Cheng // *Science* **300** (2003) 1275.

[43] X.Z. Liao, Y.H. Zhao, S.G. Srinivasan, Y.T. Zhu, R.Z. Valiev and D.V. Gunderov // *Appl. Phys. Lett.* **84** (2004) 592.

[44] X.Z. Liao, S.G. Srinivasan, Y.H. Zhao, M.I. Baskes, Y.T. Zhu, F. Zhou, E.J. Lavernia and H.F. Hu // *Appl. Phys. Lett.* **84** (2004) 3564.

[45] A.S. Argon // *Acta Mater.* **27** (1979) 47.

[46] P.S. Steif, F. Spaepen and J.W. Hutchinson // *Acta Mater.* **30** (1982) 447.

[47] B. Bokstein, V. Ivanov, O. Oreshina, A. Peteline and S. Peteline // *Mater. Sci. Eng. A* **302** (2001) 151.

[48] S.V. Bobylev, M.Yu. Gutkin and I.A. Ovid'ko // *Acta Mater.* **52** (2004) 3793.

[49] S.V. Bobylev and I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **7** (2004) 75.

[50] Y.T. Zhu, X.Z. Liao, S.G. Srinivasan, Y.H. Zhao, M.I. Baskes, F. Zhou and E.J. Lavernia *// Appl. Phys. Lett.* **84** (2004) 5049.

[51] A.A.Fedorov, M.Yu. Gutkin M.Yu. and I.A. Ovid'ko // *Acta Mater.* **51** (2003) 887.

[52] I.A. Ovid'ko and A.G. Sheinerman // *Acta Mater*. **52** (2004) 1201.

[53] I.A. Ovid'ko and A.G. Sheinerman // *Rev.Adv.Mater.Sci.* **7** (2004) 61.

[54] C.C. Koch, *Scr.Mater.* **49** (2003) 657.

[55] X. Zhang, H. Wang and C.C. Koch // *Rev. Adv. Mater. Sci.* **6** (2004) 53.
[56] A.V. Sergueeva, N.A. Mara and A.K. Mukherjee // *Rev. Adv. Mater. Sci.* **7** (2004) 67.
[57] G.-D. Zhan, J.D. Kuntz, J. Wan, A.K. Mukherjee, in *Nanostructured Materials for Structural Applications,* ed. by C. C. Berndt, T. Fischer, I. A. Ovid’ko, G. Skandan, & T. Tsakalakos (MRS, Warrendale, 2003) pp.49.
[58] Y. Wang, E. Ma, R.Z. Valiev and Y. Zhu // *Adv.Mater.* **16** (2004) 328.
[59] J. Weissmueller and J. Markmann // *Adv.Eng.Mater*. **7** (2005) 202.
[60] R.J. Asaro and S. Suresh // *Acta Mat.* **53** (2005) 3369.
[61] I.A. Ovid’ko and A.G. Sheinerman // *Acta Mater.* **53** (2005) 1347.
[62] J. Markmann, P. Bunzel, H. Roesner, K.W. Liu, K.A. Padmanabhan, R. Birringer, H. Gleiter and J. Weissmueller // *Scr.Mater.* **49** (2003) 637.