

Nanodefects in nanostructures

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ABSTRACT

The notion of nanodefects (topological defects of nanoscale translational order) in nanostructures of various types is introduced. Experimental data reported in the literature are discussed giving direct evidence for the existence of nanodefects in self-assembled periodically ordered nanostructures such as arrays of quantum dots, self-assembled superlattice films of nanoparticles, and arrays of carbon nanotubes. Also, the specific geometric features of perfect and partial cellular dislocations (being a kind of nanodefekt) and their role in superplastic deformation in nanocrystalline materials are considered.

New physical, chemical, mechanical and biological properties are exhibited by nanostructures that represent assemblies of crystallites with at least one characteristic size being of the order of a few nanometres (Chow *et al.* 2000, Gleiter 2000, Roco *et al.* 2000). Examples of such nanostructures are self-assembled ordered arrays of semiconductor quantum dots and wires (Medeiros-Ribeiro *et al.* 1998, Ross *et al.* 1998, Cui and Lieber 2001, Huang *et al.* 2001, Gudixsen *et al.* 2002), self-assembled ordered arrays of carbon nanotubes (Wei *et al.* 2002a, Zhu *et al.* 2002) and nanoparticles embedded into organic matter (Chow *et al.* 2000, Gleiter 2000, Murray *et al.* 2000, Roco *et al.* 2000), as well nanocrystalline materials which are rather irregular aggregates of nanograins (Chow *et al.* 2000, Gleiter 2000). Their unique properties are due to combined nanoscale, interface and interaction effects. The nanoscale effect occurs because many fundamental processes in solids are associated with length scales of around a few nanometres. The interface effect comes into play because a large fraction of atoms (up to 50%) of each nanosized crystallite are located at interfaces, where their behaviour is different from that in the bulk. Finally, the interaction between assembled nanosized crystallites causes unique collective properties that are more than just the sum of the properties of individual crystallites.

The spatial arrangement of nanocrystallites and their uniformity in their size and shape are among the most important issues for the combined nanoscale, interface and interaction effects that crucially affect the functional properties of nanostructures. In the first approximation, self-assembled ordered nanostructures are commonly treated as regular, periodically ordered arrays of identical nanocrystallites, in which case a theoretical description of their properties is simplified. However, real self-assembled nanostructures, as is well documented experimentally, are not regular. There are deviations of spatial positions, sizes and shapes of their structural units

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from the ideal. In addition, there are topological defects that violate nanoscale translational order inherent to self-assembled periodic nanostructures, similar to topological defects in conventional crystal lattices. For example, the symmetry of a periodically ordered nanostructure, relative to translation by a period (being commonly of the order of nanometres), is locally violated by topological defects. Examples of such topological defects are interphase-boundary-like defects in ordered assemblies of two different sizes of CdSe nanoparticles (Murray *et al.* 2000) (figure 1(a)), impurity-like defects (dome nanoislands) in ordered arrays of pyramid quantum dots (Medeiros-Ribeiro *et al.* 1998, Ross *et al.* 1998) (figure. 1(b)), impurity-like defect (double crystal) in a chain of nanoparticles in magnetostatic bacteria (Dunin-Borkowski *et al.* 2001) (figure 1(c)), vacancy-like defects in self-assembled superlattice films of FePt nanoparticles with non-perfect chemical ordering (Harrell 2001) (figure 1(d)), carbon nanohorns (Ajayan *et al.* 2002), X-, Y- and T-like junctions of carbon nanotubes (Terrones *et al.* 2002) (figure 1(e)), and interstitial-like defects in lithographically synthesized supramolecular pillar array in thin polymer melts (Chou and Zhuang 1999) (figure 1(f)). With a generic definition as *topological defects of nanoscale translational order* inherent to nanostructures, we shall call such defects *nanodefects*.

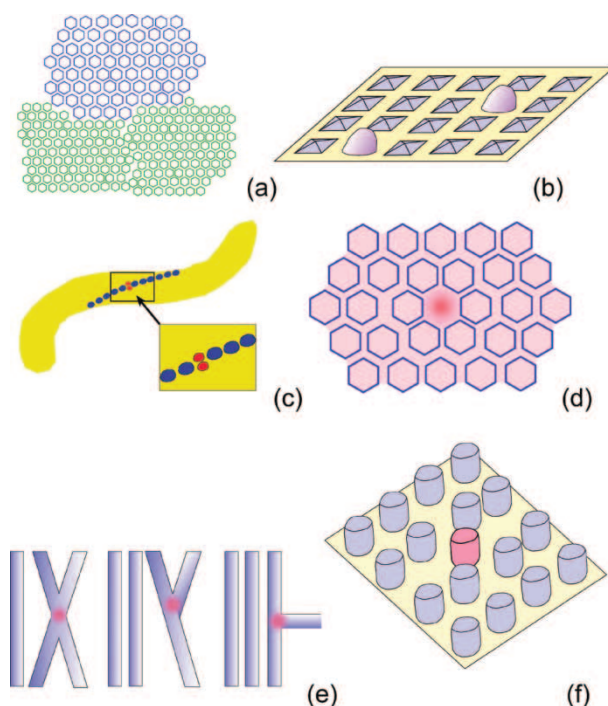


Figure 1. Nanodefects in ordered nanostructures (schematically). (a) interphase-boundary-like defect in ordered assemblies of two different sizes of CdSe nanoparticles; (b) impurity-like defects (dome nanoislands) in ordered arrays of pyramid quantum dots; (c) impurity-like defect (double crystal) in a chain of nanoparticles in magnetostatic bacteria; (d) vacancy-like defect in self-assembled superlattice film of FePt nanoparticles; (e) X-, Y- and T-like junctions of carbon nanotubes; (f) interstitial-like defect in lithographically synthesized supramolecular pillar array in a thin polymer melt.

Nanodefects are formed during the fabrication and processing of nanostructures under highly non-equilibrium conditions. In some cases, they are capable of strongly influencing the behaviour of ordered nanostructures. For instance, the formation of impurity-like defects (dome nanoislands) in ordered arrays of pyramid quantum dots dramatically breaks the uniformity of quantum dots in size and shape, giving rise to degradation of their functional characteristics highly desired for applications (Medeiros-Ribeiro *et al.* 1998, Ross *et al.* 1998). In general, new properties of nanostructures may arise owing to the presence of nanodefects. For instance, carbon nanotubes with such nanodefects as Y- and T-like junctions could act as multi-terminal electronic devices (Dunin-Borkowski *et al.* 2001).

Also, the notions of perfect and partial cellular dislocations (CDs) (kinds of nanodefect) in arrays of nanograins are effective in a description of the experimentally observed (McFadden *et al.* 1999, Mohamed and Li 2001, Valiev *et al.* 2001, Mukherjee 2002) superplasticity of nanocrystalline materials. In fact, following theoretical representations (Zelin and Mukherjee 1993, 1995, Zelin *et al.* 2001), superplastic deformation occurs via movement of perfect CDs that are topological dislocations in arrays of grains. A perfect CD is illustrated in a two-dimensional model array of hexagonal nanograins as a dislocation with a pair of five- and seven-sided nanograins representing its core (figure 2(a)). In the case of nanocrystalline materials, a CD locally (at the dislocation core) violates nanoscale translational order inherent in a periodic array of nanosized grains (figure 2(a)) and, by the definition given in this letter, represents a nanodefect. The Burgers vector of the

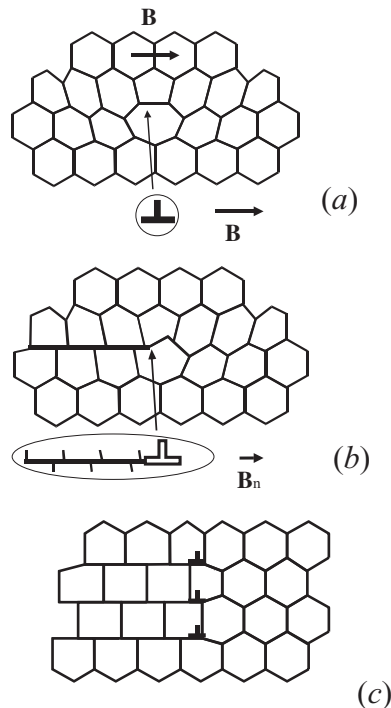


Figure 2. CDs in nanocrystalline materials. (a) perfect and (b) partial CDs in a regular array of hexagonal nanograins (cells); (c) movement of group of partial CDs which causes plastic deformation localized within a shear band.

perfect CD shown in figure 2(a) is \mathbf{B} , the lattice vector of the periodic array of regular hexagonal nanograins which plays the role of the reference lattice. The essential role of CDs in superplasticity is supported by experimental observations of inhomogeneities of the plastic shear along the regions where superplastic deformation is localized (see Zelin and Mukherjee (1993, 1995), Zelin *et al.* (2001) and references therein).

However, the experimental data discussed do not distinguish the type, perfect (figure 2(a)) or partial (figure 2(b)), of CDs that are carriers of superplastic deformation. A partial CD in the model array of nanograins violates the nanoscale translational order, not only locally at the dislocation core but also at the stacking-fault surface formed behind the moving dislocation (figure 2(b)). Such dislocations are similar to partial dislocations in conventional crystals, say, polar semiconductors with hexagonal crystal lattices (Benetto *et al.* 1997, Nunes *et al.* 1998, Ovid'ko 2002a, Ovid'ko and Sheinerman 2002), high- T_c superconductors (Kung *et al.* 2001, Gutkin and Ovid'ko 2001) and quasicrystals (Ovid'ko 1992, Caillard *et al.* 2000). Since these CDs are partial, their Burgers vectors are not lattice vectors of the periodic array (lattice) of regular hexagonal nanograins (figure 2(b)). Movement of partial CDs causes plastic deformation of a nanocrystalline sample and changes its structure behind the moving dislocations (as shown in figure 2(b) and (c) and considered in more detail below).

In general, the discussed representations on perfect and partial CDs are useful in analysis of the specific peculiarities of plastic deformation in nanocrystalline materials at the nanoscale level. They serve as complementary to representations on deformation mechanisms (lattice dislocation slip (Pande *et al.* 1993, Pande and Masumura 1996), grain-boundary diffusional creep (Masumura *et al.* 1998, Kim *et al.* 2000, Yamakov *et al.* 2002), triple-junction diffusional creep (Fedorov *et al.* 2002), grain boundary sliding (Hahn *et al.* 1997, Hahn and Padmanabhan 1997, Fedorov *et al.*, 2003) and rotational deformation (Gutkin *et al.* 2002, Murayama *et al.* 2002, Ovid'ko 2002b), which are commonly described on an atomic length scale in terms of defects of atomic structures, with subsequent extrapolation to a description of their contributions to the macroscopic deformation behaviour of a nanocrystalline specimen as a whole. More precisely, in the framework of the combined atomic-level, nanoscale and macroscopic approach to a description of plastic flow in nanocrystalline materials, the atomic-level deformation mechanisms provide local plastic deformation and changes in grain shapes in the cores of moving CDs, movement of individual CDs causes nanoscale plastic deformation within shear bands, and evolution of CD groups (say, CD pile-ups each being associated with a shear band) causes macroscopic deformation of a nanocrystalline sample as a whole.

We shall use the combined approach in both a qualitative description of the behaviour of imperfect CDs and a comparison of the contributions of perfect and imperfect CDs to experimentally observed localization of (super)plastic flow in nanocrystalline materials. To do so, we first discuss the behavioural features of perfect CDs. Following Zelin and Mukherjee (1993, 1995) and Zelin *et al.* (2001), movement of a perfect CD assumes correlated grain movement and topological changes in grain shapes within the CD core, while grains outside the core region are only elastically strained. In this situation, the energy barrier for perfect CD movement is caused by topological changes in grain shapes, which repeatedly occur in a reversible manner at every elementary transfer of the perfect CD by a distance close to the grain size. (This barrier is an analogue of a Peierls barrier for

movement of conventional lattice dislocations in crystals.) In doing this, movement of a perfect CD along a shear surface does not enhance or hamper movement of other CDs along the same shear surface. It causes difficulties in explaining the experimentally detected (Niemann *et al.* 1991, Carsley *et al.* 1995, Witney *et al.* 1995, Andrievskii *et al.* 1997, Andrievskii 1998, Wang *et al.* 2002, Q. Wei *et al.* 2002b) (super)plastic flow localization in nanocrystalline materials, in terms of perfect CDs.

Movement of a partial CD is accompanied by irreversible topological changes in nanograin shapes at a stacking-fault surface (figure 2 (b) and (c)). In the framework of the combined atomic-level and nanoscale approach, the nanoscale changes (figure 2 (b) and (c)) are effectively described as those associated with numerous atomic-scale transformations of groups of conventional grain-boundary dislocations (carriers of grain-boundary sliding), lattice dislocations and point defects in nanoscale cores of partial CDs in mechanically loaded nanocrystalline materials. With the focus of this letter being placed on superplastic deformation occurring mostly through grain-boundary sliding, we consider a first-approximation model that qualitatively describes a partial CD as a localized pile-up of conventional grain boundary dislocations exhibiting a correlated behaviour under the action of mechanical stresses. In the framework of the model, the generation and movement of partial CDs are processes associated with transformations of grain-boundary dislocations at CD cores. Conventional grain-boundary dislocations are generated under shear stress action at the sample free surface and move along the grain-boundary (figure 3 (a)). They form a pile-up stopped at a triple junction where grain-boundary planes change their orientation (figure 3 (a)), causing a geometric obstacle for grain-boundary dislocation movement. The pile-up of conventional grain-boundary dislocations, in a first approximation, is equivalent to an imperfect CD. Its Burgers vector \mathbf{B}_n is equal to the sum of Burgers vectors \mathbf{b}_i of grain-boundary dislocations composing the pile-up: $\mathbf{B}_n = \sum_i \mathbf{b}_i$ (figure 3 (a)). (Note that the equation $\mathbf{B}_n = \sum \mathbf{b}_i$ provides the relationship between nanoscale and atomic-level models of plastic deformation, based on the geometry of partial CDs and grain-boundary dislocations.) When the shear stress reaches some critical value, the grain-boundary dislocation pile-up (partial CD) moves across the triple junction (figure 3 (b)) and its neighbouring triple junctions (figures 3 (d)–(f)). Movement of the pile-up (partial CD) across triple junctions of grain-boundaries gives rise to transfer of the triple junctions (figures 3 (b)–(f)) by vectors that are the sum of the Burgers vectors of the dislocations that form the pile-up. Thus, movement of grain-boundary dislocations leads to changes in the topological structure of the nanograin ensemble. In order to minimize the total length of grain boundaries, their local migration restores the topological structure of the ensemble (figures 3 (c)–(f)). As a result of numerous acts of movement of grain-boundary dislocations across triple junctions and accompanying grain-boundary migration, grain-boundary planes become tentatively parallel each other at the shear surface (figure 3 (e)–(f)). In these circumstances, triple junctions stop being geometric obstacles for movement of new grain-boundary dislocations (figures 3 (e) and (f)), which is thereby enhanced along the shear surface. Thus, movement of grain-boundary dislocations in local regions of a mechanically loaded nanocrystalline material gives rise to the softening of these regions. In terms of CDs, movement of partial CDs is accompanied by stacking-fault formation that enhances movement of new partial CDs (figure 3).

Note that, in contrast with conventional partial dislocations that often form pairs equivalent to perfect lattice dislocations in crystals, partial CDs do not form

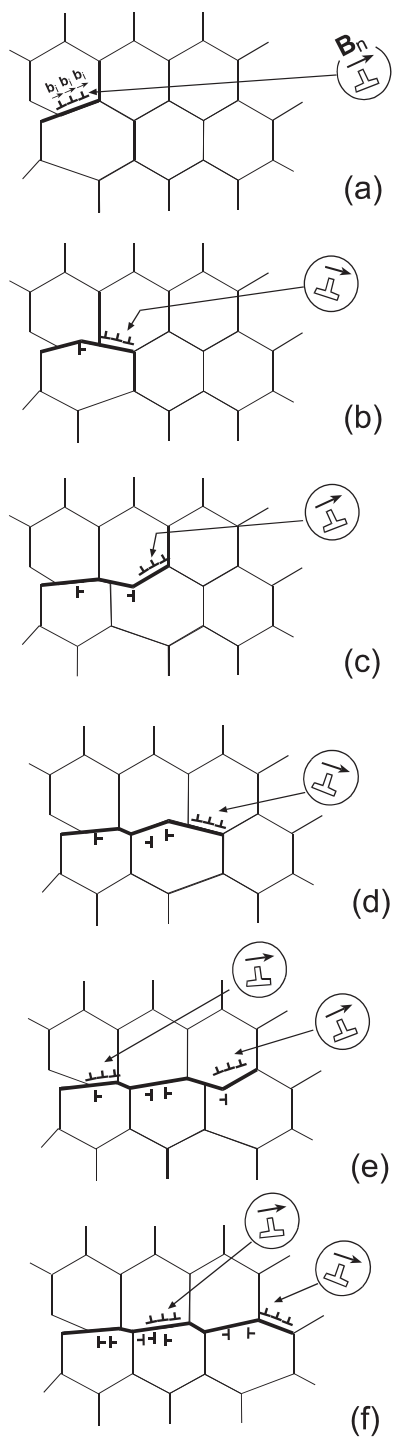


Figure 3. Movement of grain boundary dislocation pile-ups serving as atomic-level models of nanoscale partial CDs in nanocrystalline materials (see text).

pairs equivalent to perfect CDs. They are joined by stacking faults with the only sample free surface. As the discussed representations on the softening mechanism (figure 3) are inherent to movement of only partial CDs (and absent in the case of perfect CDs) they allow one to describe effectively the experimentally detected (Niemann *et al.* 1991, Carsley *et al.* 1995, Witney *et al.* 1995, Andrievskii *et al.* 1997, Andrievskii 1998, Wang *et al.* 2002, Wei *et al.* 2002b) (super)plastic flow localization in nanocrystalline materials. Note that, following electron microscopy experiments (Wei *et al.* 2002b), shear bands in nanocrystalline materials contain brick-like grains with grain boundaries parallel to and perpendicular to the shear direction. It is in good agreement with our model of the stacking fault structure formed behind moving partial CDs (figures 2(b) and (c) and 3).

Movement of partial CD is accompanied not only by softening but also by strengthening, owing to transformations of grain-boundary dislocations composing nanoscale cores of partial CDs. In fact, for geometric reasons, gliding grain-boundary dislocations change the orientation of their Burgers vectors at triple junctions of grain boundaries (figure 3). With the Burgers vector conservation law, residual sessile dislocations are formed at triple junctions (figure 3). These dislocations elastically interact with new grain-boundary dislocations moving towards the sessile dislocations (figures 3 (e) and (f)), in which case the strengthening comes into play (for details, see Fedorov *et al.* 2003, Gutkin *et al.* 2003). In terms of CDs, this strengthening is related to transformations of partial CD cores and the stacking-fault structures.

Thus, there are both softening and strengthening effects occurring as a consequence of nanoscale transformations in cores of moving partial CDs (figure 3). In addition, there are softening and strengthening effects at the macroscopic level, which are caused by the long-range elastic interaction between CDs. We think that the competition between the softening and strengthening effects at the nanoscale and macroscopic levels causes the superplastic deformation behaviour of a mechanically loaded nanocrystalline solid. A detailed qualitative analysis of the specific features of superplastic deformation in nanocrystalline materials in terms of CDs is beyond the scope of this letter. Below we shall just briefly discuss this subject, using the idea of the competition between nanoscale and macroscopic softening and strengthening effects.

Superplastic deformation occurs in nanocrystalline materials commonly at high strain rates and low temperatures, compared with their coarse-grained counterparts (McFadden *et al.* 1999, Mohamed and Li 2001, Valiev *et al.* 2001, Mukherjee 2002). Typical stress–strain curves for nanocrystalline materials under high-strain-rate superplastic deformation show an extensive region of strain hardening with extremely high values of the peak flow stress (Valiev *et al.* 2001, Mukherjee 2002). This feature, which is unusual for conventional low-strain-rate superplasticity, is qualitatively described in terms of CDs as follows. Isolated CDs are generated and move under a mechanical load in nanocrystalline materials at the initial stage of superplastic deformation. They are highly distant from each other, in which case the flow stress is caused only by nanoscale structural transformations (figure 3) in cores of individual CDs. Superplastic deformation occurs if nanoscale strengthening dominates over nanoscale softening until the deformation stage at which the density of partial CDs is high. This nanoscale strengthening prevents necking and is responsible for an increase in the flow stress that drives the movement of individual partial CDs. With increasing plastic strain, nanoscale structural transformations

(figure 3) in cores of individual CDs make grain-boundary planes tentatively parallel to each other. In doing so, the nanoscale softening becomes essential. However, the density of CDs increases with increasing plastic strain. If the density is high, the long-range elastic interaction between CDs comes into play, causing an increase in the flow stress with increasing dislocation density. Similar to conventional dislocations (for example Hirth and Lothe (1982)), the flow stress is increased by interactions according to $\Delta\sigma \propto \rho^{1/2}$, where ρ is the CD density. This macroscopic strengthening prevents necking and allows a nanocrystalline sample to undergo large deformations. The flow stress increases up to point where the nanoscale softening becomes dominant over the nanoscale strengthening. At this point, movement of new CDs is highly enhanced along the shear surfaces where previous CDs have moved. As a corollary, the formation of CD pile-ups intensively occurs and this is accompanied by a macroscopic softening due to stress concentration near the CD pile-up heads. When the macroscopic softening becomes dominant over the macroscopic strengthening, it leads to the neck formation followed by failure. Thus, the above scenario of evolution of partial CDs qualitatively describes typical stress-strain curves of nanocrystalline materials under superplastic deformation.

In summary, we have suggested a generic definition of nanodefects in diverse nanostructures as 'topological defects violating nanoscale periodic translational order inherent to nanostructures'. Analysis of data in the literature shows that nanodefects are experimentally found in diverse, periodically ordered nanostructures where they are capable of strongly influencing properties of nanostructures. In particular, the experimentally detected localization of (super)plastic flow in nanocrystalline materials is effectively described as that occurring via movement of groups of imperfect CDs (a kind of nanodefekt). In the context discussed, identification and systematic study of nanodefects in nanostructures are important for both understanding the fundamentals of the combined nanoscale, interface and interaction effects and development of current and novel technologies exploiting nanostructures. Use of the notion of nanodefects may allow researchers involved in science and engineering of different nanostructures to share views and develop interdisciplinary ideas.

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