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Review

Emission of Dislocations from Grain Boundaries and Its Role in Nanomaterials

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Abstract: The Frank-Read model, as a way of generating dislocations in metals and alloys, is widely accepted. In the early 1960s, Li proposed an alternate mechanism. Namely, grain boundary sources for dislocations, with the aim of providing a different model for the Hall-Petch relation without the need of dislocation pile-ups at grain boundaries, or Frank-Read sources inside the grain. This article provides a review of his model, and supporting evidence for grain boundaries or interfacial sources of dislocations, including direct observations using transmission electron microscopy. The Li model has acquired new interest with the recent development of nanomaterial and multilayers. It is now known that nanocrystalline metals/alloys show a behavior different from conventional polycrystalline materials. The role of grain boundary sources in nanomaterials is reviewed briefly.

Keywords: dislocation emission; grain boundaries; nanomaterials; Hall-Petch relation; metals and alloys

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1. Introduction

To explain the properties of crystalline aggregates, such as crystal plasticity, Taylor [1,2] provided a theoretical construct of line defects in the atomic scale of the crystal lattice. With the use of the electron microscope, the sample presence of dislocations validated Taylor's theory. However, the questions remained on the source of dislocations and the conditions required for their generation and migration in the crystal. While Frank and Reed [3] presented a mechanism to show the generation of many dislocations when the crystal is subjected to an applied stress, electron microscopic observations provided the support for the proposed mechanism. The rare observation of the Frank-Read (FR) source could not be justified for the large density of dislocations seen in crystals.

Li [4] was the first to recognize this issue and put forth the concept of grain boundary ledges as sources for dislocations. Li proposed the emission of dislocations from grain boundary ledges of the type shown in Figure 1. He assumed that the density of ledges is about the same in the grain boundary, which implies that fine-grained materials have a greater dislocation density when they yield. Since then, there have been numerous confirmations of grain boundary dislocation sources under an applied stress or fluctuation of temperature. Direct evidence of these ledges has been found using transmission electron microscopy (TEM).

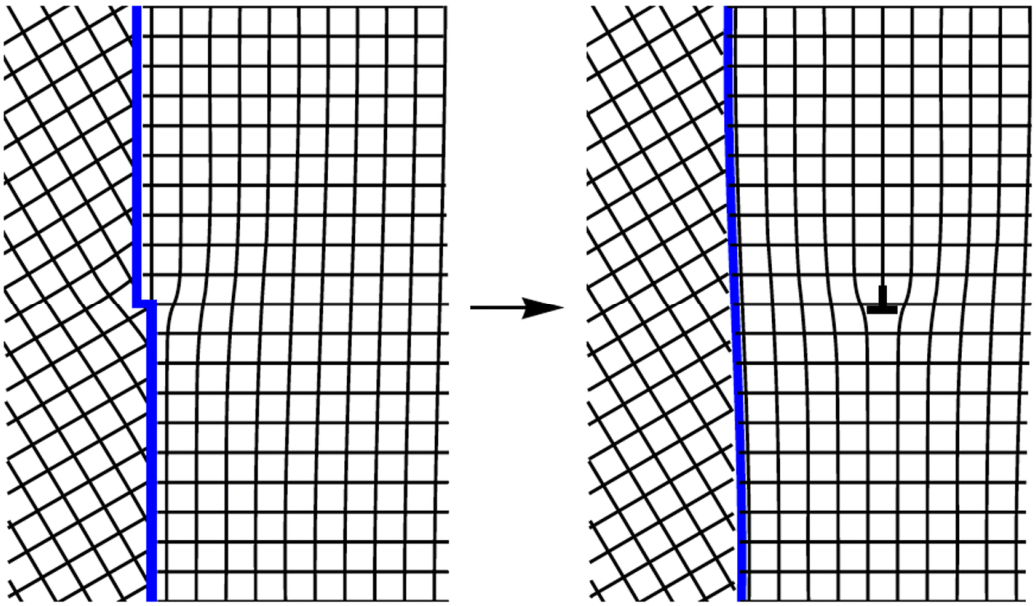

Figure 1. Grain boundary ledge model. (Schematic diagram) From Li [4].

Hall-Petch (HP) relation and the pile-up model were originally developed for iron and used the concept of pile-up of dislocations, originating from the Frank-Read source. Pile-up model has been frequently quoted to explain the HP relationship in other materials. However, it is somewhat ironic that the Frank-Read source and dislocation pile-ups were rarely, if ever found in iron. Li proposed the grain boundary source model. He has considered that dislocations are generated at grain boundary (GB) ledges and all of these dislocations migrate to dislocation forests in grain interiors. Li assumed that the density of ledges is about the same in the grain boundary, so the dislocation density will scale inversely with grain size. Dislocation density also scales as square of yield stress. The two relations, when combined, give the well-known Hall-Petch relation. In fact, Li compared the magnitude of stress in his model with that of the pile-up model with a reasonable agreement.

Ashby [5] described polycrystals as plastically non-homogeneous materials in which each grain deforms by different amounts, depending on its orientation and the constraints imposed by neighboring grains. If each grain were forced to undergo the same uniform strain, voids would form at grain boundaries. To avoid the creation of voids, and ensure strain compatibility, dislocations are introduced. Voids can be corrected by the same process by dislocations of opposite signs. Ashby [5] showed that the number of geometrically necessary dislocations (GNDs) generated at the boundaries and pumped into the individual grains is roughly De/4b, where D is the grain diameter, e is the average strain, and b the magnitude of the dislocation Burgers vector. In both two- and three-dimensional arrays of grains, this leads to a density of geometrically necessary dislocations. These geometrically necessary dislocations can be the origin of the grain size dependence of work-hardening in polycrystals. If it is assumed that hardening depends only on average dislocation density, then this approach yields a $\sigma \sim D^{-1/2}$ law for grain boundary hardening, where σ is the yield stress. The concept of generating geometrically necessary dislocations to ensure strain compatibility in polycrystalline materials eliminates the necessity to consider dislocation pile-ups to rationalize the flow of the stress-grain size relationship. It suggests that grain interiors behave essentially like single crystals of the same orientation deforming by single slip while the regions on either side of the grain boundaries undergo lattice rotation and secondary slip. This, in fact, has been observed experimentally by Essmann, et al. [6]. Emission of geometrically necessary dislocations occurs from the grain boundary, which must act as a major source of dislocations.

A comprehensive review of Li's model, its experimental verification, and its comparison with Frank-Read (FR) source models, especially pile-up models, have been given by Murr [7]. A more recent review of Li's model and its implications, vis-a-vis Hall-Petch relation, is also given by Naik and Walley [8]. They reviewed some of the factors that control the hardness of polycrystalline materials with grain sizes less than 1 μm, especially the fundamental physical mechanisms that govern the hardness of nanocrystalline materials. For grains less than 30 nm in size, there is evidence for a transition from dislocation-based plasticity to grain boundary sliding, rotation, or diffusion as the main mechanism responsible for hardness. However, we disagree with their conclusion that the evidence surrounding the inverse Hall-Petch phenomenon is inconclusive, and can be due to processing artefacts, grain growth effects, and errors associated with the conversion of hardness to yield strength in nanocrystalline (NC) materials. The inverse Hall-Petch phenomena is now well established and subject of numerous theoretical and experimental studies. For a review, see reference [8,9]. There were some doubts about its validity in early years when the specimens tested were not fully dense or had other defects. The role of dislocations in fine grain and nanomaterials has renewed interest in the concept of GB as source of complete or partial dislocations. It was found that for most metals with grain sizes in the nanometer regime, experiments have suggested a deviation away from the HP relation relating yield stress to average grain size (It is not clear if such deviations are a result of intrinsically different material properties of nanocrystalline (NC) systems or due simply to inherent difficulties in the preparation of fully dense NC samples and in their microstructural characterization. For a detailed discussion on classical HP and Inverse HP models see the review by Pande and Cooper [9] Therefore, we will not go into the details of Li's model, except for the case of fine-grained materials, where GB sources may play a prominent role.

The use of large-scale molecular dynamics (MD) in the study of the mechanical properties of NC materials provides a detailed picture of the atomic-scale processes during plastic deformation at room temperature. Using an MD model performed at room temperature, it is suggested that the GB accommodation mechanism can be identified with GB sliding, triggered by atomic movement and to some extent stress assisted diffusion [10].

We will briefly consider these issues in subsequent sections.

2. Modeling and Simulation of Dislocations from Grain Boundaries

Computer modeling of dislocations of dislocation emission from grain boundaries has been extensively studied in recent years. Excellent work can be attributed due to Yamakov et al. [10]. Using MD simulation, they examined the nucleation of extended dislocations from the GBs in NC aluminum. They showed the length of the stacking fault connecting the two Shockley partials that form the extended dislocation, i.e., the dislocation splitting distance, r_{split}, depended not only on the stacking-fault energy but also on the resolved nucleation stress. Their simulations were only for columnar grain microstructures with a grain diameter, d, of up to 70 nm. The magnitude of r_{split} relative to d was found to represent critical length scale controlling the low-temperature mechanical behavior of NC materials. They, thus, confirmed that the mechanical properties of NC materials, such as the yield stress, depend critically on the grain size.

It was shown that under high stresses, needed to nucleate extended dislocations from GBs, the magnitude of r_{split} can be significant, particularly in a NC fcc metal. In fact, it becomes comparable to the grain size, d. Thus, the splitting distance can be considered as a new length scale, in addition to d. A complete extended dislocation cannot be nucleated unless $d > r_{split}(\sigma)$. Therefore, it appears to be a necessary condition for the dislocation–glide mechanism to operate in a NC fcc metal. The authors have beautifully demonstrated the interplay between these two length scales and their effect on the mechanical properties of NC materials.

Recent simulations have confirmed the important role dislocations are expected to play in the deformation of NC fcc metals [11–13]. However, it should be noted that for the

rather small grain diameters (of up to 12 nm) considered in these simulations, single partials produce stacking faults as they glide through the grain and become incorporated into the GBs. These stacking faults remain in the grains as planar defects which are not recovered. This process, most likely, will only operate during the initial stages of deformation, and is quite different from the usual slip mechanism in materials with large grain sizes. The largest grain sizes considered in these simulations was of d = 12 nm) [13], and there, the dislocations could account for only about 30% of the total deformation, and for even smaller grain sizes, practically no dislocations were observed. No dislocations were observed in grains smaller than 8 nm. What was the dominant deformation mechanism observed? Most MD simulations involved GB-mediated processes, such as GB sliding [11–13] or GB diffusion [14–16]. Although most of the studies of inverse HP has been for fcc metals there is no reason to believe that it will not apply to other structures. The role of dislocations coming from the Frank-Read (FR) source diminish as grain size decreases, discussed in detail in reference 9 and 45. For grain sizes below 12 nm, the only dislocation source active would be at grain boundaries.

In recent years, the interaction of dislocations with GBs has been subject of both experimental and theoretical studies. The theoretical work of Li led to the conclusion that the nucleation of a dislocation on a GB requires GB ledges [4,13]. On the other hand, experimental studies of the plastic deformation of polycrystals at low temperatures suggested that GBs become the dominant dislocation sources for relatively small grain sizes. The nucleation process may be expected to be independent of grain size [13,16]. Therefore, it is expected that the GBs should provide the necessary dislocation sources at least for the low-temperature deformation of NC materials. Hence, at the relatively high stresses required for the nucleation process, the dislocation-glide mechanism should, in principle, take place even in NC materials. For details of their simulation procedure in NC metals with columnar microstructure, see reference [17].

The process briefly is: (1) at a high enough stress, only a single 1/6 [112] partial is nucleated from a GB or a triple junction. (2) This partial dislocation, while still attached to GB, glides through the interior of the grain, connected to the GB by the stacking fault left behind by the glide. (3) For large grains, dislocation is annihilated at the opposite GB before a second partial can be formed, and a stacking fault transecting the entire grain remains. (4) If the grain is large enough, the energy of the propagating stacking fault eventually becomes too high and a second partial is nucleated to terminate the stacking fault; together with the first partial, an extended 1/2 [110] dislocation is thus formed.

It should be stated that only if the grain size is large enough [16] for the slip mechanism by dislocation glide to be fully developed, conventional HP hardening should occur due to the retarding effect of pile-ups. For the formation of these pile-ups in NC materials, and their effect on the HP mechanism, see reference [18–20]. It is shown that interaction between two extended dislocations should lead to another length scale—the critical distance for a dislocation pile-up—above which one can expect to observe the HP effect. Thus, it is clearly demonstrated that at such small grain sizes even a single complete extended dislocation is not expected. All of this leads us to conclude that when grain sizes are in nanoscale, the dominant sources of the dislocations are grain boundaries and FR mechanism is not present.

An important contribution to this field is the work of Borovokov [21]. In this MD study, they demonstrate that one of the mechanisms that can play an important role in the strength and plasticity of metallic polycrystalline materials is the heterogeneous nucleation and emission of dislocations from GB. This was done by considering the dislocation nucleation from copper bi-crystal with a number of $\langle 110 \rangle$ tilt GBs. These GBs covered a wide range of misorientation angles. It is conclusively shown that the mechanic behavior of GBs and the energy barrier of dislocation nucleation from GBs are closely related to the lattice crystallographic orientation, GB energy, and the intrinsic GB structures. Thus, one can conclude that atomistic analysis of the nucleation mechanisms can provide the exact

mechanism of this kind of nucleation and emission process, and that can help us to better understand the role of GBs as a dislocation source. For details, see also reference [22].

We should also mention, in this context, a theoretical model that has been developed by Li et al. [23]. It deals with the effect of shear-coupled migration of grain boundaries on dislocation emission in NC materials. They showed that the dislocation emission can be enhanced considerably as shear-coupled migration. They also discuss factors that can lead to an optimal dislocation emission. Their conclusions have been confirmed quantitatively by the existing MD simulations based on the results of Shiue and Lee [24].

3. Experimental Verification of Dislocation Emission

We briefly mentioned before the use of TEM in thin films for detecting evidence of dislocation emission from GBs. Additionally, a brief description is given of the experiments, which were conducted to observe in-situ dynamics of dislocation emission from GBs for bulk specimens at elevated temperatures. An uncommonly known technique of photo-emission was used. The instrument used for this purpose, is known as the photo emission electron microscope (PEEM). A brief description of the instrument and an electron micrograph are presented below. Details of the experiment is reported by Li et al. [25]. A schematic diagram of PEEM is shown in Figure 2.

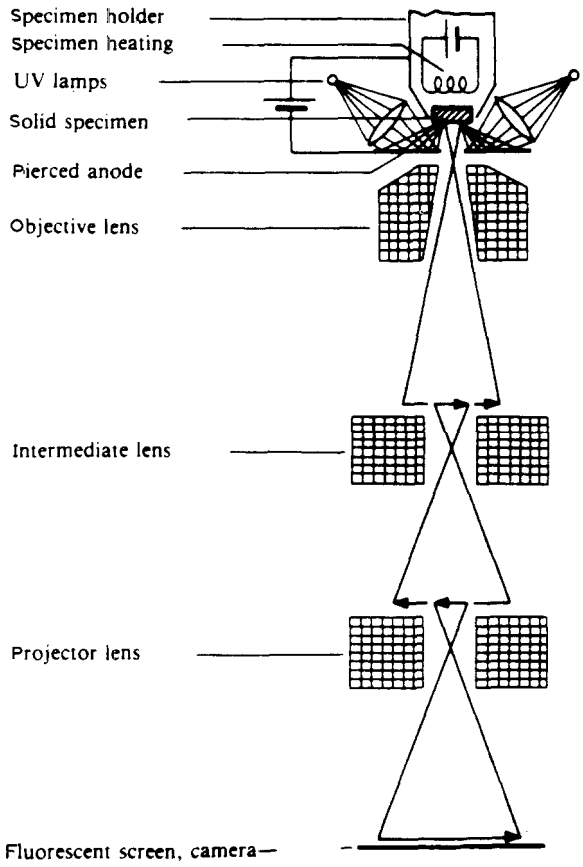

Figure 2. Schematic diagram of photoelectron emission microscopy.

A cylindrical sample of a titanium alloy was used as the target in the electron optical system. The sample was heated to a predetermined temperature. It served as a cathode in the electron accelerating field. A three-stage lens system of the microscope, as shown in Figure 2, was used to image the emitting photoelectrons on to a fluorescent screen, and recorded by a video camera, along with a television monitor. Details of the instrument and its applications are described elsewhere [26–35]. This system allows continuous monitoring of changes in the microstructure, in in bulk samples, up to a temperature of 1500 °C. Prior

to the photo-electron emission experiment, the polished surface of the sample was cleaned by bombarding argon at a glancing angle, conducted in an adjoining chamber. The intensity of emitted electrons is a function of the crystallographic orientations, chemical composition of the sample, and surface topography, during heating or cooling, at a temperature above the transformation of the titanium alloy. A bulge emerging from the boundary appeared, as shown in Figure 3.

Figure 3. A bulge formed at a grain boundary of β-Ti6A1-2V-6Zr alloy during rapid heating (photoemission electron microscope PEEM).

The contrast seen in Figure 3 is interpreted as emission of defects from grain boundary ledges. Details of these observations are presented in [25].

Autruffe et al. [36], using TEM, with samples subjected to uniaxial tensile straining showed that dislocation profiles extending from the GBs, and associated with ledges on the boundary plane, increased in frequency with increasing strain. They conclude that GBs are the principal sources for dislocations. In these observations, dislocation profiles resembling dislocation pile-ups were directly observed to form at GB ledges.

Similar and very extensive direct experimental evidence of dislocation emission from GBs have been provided by Murr and his coworkers [7], showing dislocation emission from GB ledges in 304 stainless steel. (see Figure 4).

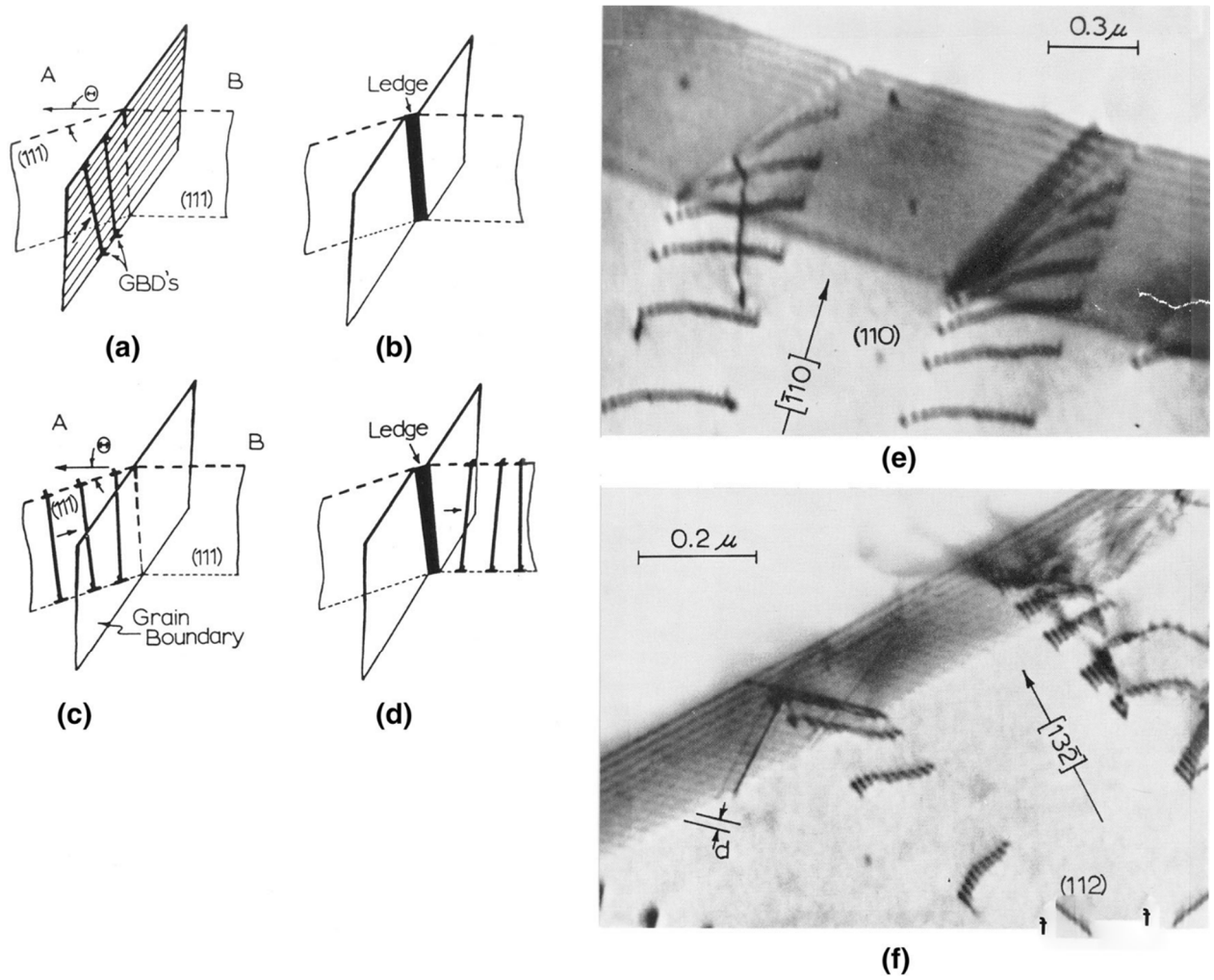

Figure 4. (**a**–**d**) schematics of grain boundary ledge formation, and (**e**,**f**) showing dislocation emission from grain boundary ledges in 304 stainless steel. From Murr [7].

4. Effects of Grain Boundary Disorder and Impurities on Dislocation Emission

Very small amounts of immiscible solutes can dramatically decrease the ability of dislocations to nucleate from GBs. It was recently reported [37] that segregation of Zr to GBs in nanocrystalline (NC) Cu can lead to the development of disorder in the intergranular structure. In this study, the authors employ atomistic computer simulations to investigate how this disorder affects dislocation nucleation from the GBs under applied stress. It was found that a fully disordered GB structure suppresses dislocation emission and significantly increases the yield stress.

The results of the MD simulations [38], which show that, at larger concentrations, the solute effect becomes non-trivial: there are concentration ranges where even a small addition of solutes considerably suppresses the dislocation nucleation from grain boundaries, and there are concentration ranges where the addition of new solutes almost does not change the dislocation nucleation. The authors also provide an atomic mechanism of these effects [38].

Solute additions are commonly used to stabilize NC materials against grain growth and can simultaneously enhance the strength of the material by impeding dislocation emission from the GBs. In this study [38], the authors demonstrate using molecular dynamics (MD) simulations that the effect of solutes on dislocation nucleation depends on the distribution of solutes at the GB. Solutes with a smaller positive size mismatch to the host can be more effective in suppressing dislocation emission from GBs, in comparison

to others that have larger mismatch. These findings are relevant to the search for optimal solute additions, which can strengthen NC material by suppressing the nucleation of dislocation slip from GBs, while stabilizing it against grain growth.

Another study [39] reports using atomic simulation on GB dislocation sources in NC copper. The authors provide an insight into dislocation sources in NC copper. Atomistic studies of this type provide details of the emission sequence that enhance understanding of dislocation sources in high angle boundaries.

A three-dimensional model for the generation of split dislocations by GBs in NC Al is proposed in reference [40]. In terms of this model, rectangular glide split-dislocation half-loops nucleate at glide lattice dislocation loops pressed to GBs by an applied stress. The level of the applied stress and the grain size at which the emission of such dislocation half-loops becomes energetically favorable are determined.

A theoretical model is suggested that describes the emission of partial Shockley dislocations from triple junctions of GBs in deformed NC materials [41]. In the framework of the model, triple junctions accumulate dislocations due to GB sliding along adjacent GBs. The dislocation accumulation at triple junctions causes partial Shockley dislocations to be emitted from the dislocated triple junctions and, thus, accommodates GB sliding. Ranges of parameters (applied stress, grain size, etc.) are calculated, in which the emission events are energetically favorable in NC Al, Cu and Ni. The model accounts for the corresponding experimental data reported in the literature.

Finally, it is worth mentioning the work of Swygenhoven et al. [42], which deals with the atomic mechanism responsible for the emission of partial dislocations from GB in NC metals. It is shown that, in a 12 nm grain-size sample, GBs containing grain-boundary dislocations (GBDs) can emit a partial dislocation during deformation by local shuffling and stress assisted free-volume migration.

5. Dislocation Emission from Grain Boundaries in Nanocrystalline Materials

Finally, utilizing the brief discussion provided in previous sections we consider the Dislocation Emission from GBs in NC materials in some detail. Rapid development of NC materials has raised the question of the role that dislocation pile-ups and other modes of dislocation production play in determining the strength of the materials, vis-a-vis the HP effect. For this purpose, we divide the region in two subsections. First, we consider deformation mechanisms, ultrafine grains, typically between 20 to 100 nm, and later grains finer than that.

5.1. Deformation Mechanisms Ultrafine Grains

In this section, we consider grain sizes in the intermediate range, i.e., between 20 and 100 nm, where a departure from classical HP is first noticed. Even in nanoscale some features of pile-up characteristics are applicable, and can have a significant effect. These include the effect of a small number of dislocations, a continuum versus discrete crystal dislocation description and the influence of elastic anisotropy. For a detailed history of the first 60 years of HP relation, see the excellent review by Armstrong [43]. It is seen that, usually the pile-up of dislocations at GBs is envisioned as the key mechanism, which causes strength increase by grain refinement. However, several models predict the breakdown of the pile-up mechanism in NC metals. With even further grain refinement, some experiments evidence softening of the material (for a review see [9,44,45]). The HP effect is normally explained by appealing to dislocation pile-ups near the grain boundaries. Once the grain size drops below the equilibrium distance between dislocations in a pile-up, pile-ups are no longer possible, and the HP relation should cease to be valid. For example, Pande, Masumura and Armstrong 1993 [46] following the dislocation pile-up model proposed by Pande et al. (see reference [9]), estimated that about ten dislocations can be stored in the approximately 100 nm Au or Cu grains. Such short dislocation pile-ups may not easily induce enough shear stress concentration to break through the grain, although it can accommodate a certain extent of plastic strain.

Using the dislocation pile-up model for the HP relation, Armstrong [47] examined ultrafine grain sizes when only a few dislocations were involved in the pile-up, which were formed at applied stress levels close to the theoretical limit. Each dislocation added to the pile-up contributes a step reduction in the HP stress. Consequently, differences in dislocation configurations and types of pile-ups are easily recognized in the limit of small dislocation numbers.

Even if the micro grains only have a few dislocations, the source of the dislocations are not established with certainty. FR sources in such small spaces seems unlikely. Could they come from the GB? We know that the GBs certainly play a role in determining properties of metallic materials. For example, dislocation-GB interactions, GB sliding grain rotation, GB diffusion, and GB migration all influence mechanical properties of polycrystalline materials. In this region they may also provide the small number of whole dislocations needed in the models discussed above.

Typically, the HP plot is divided into three regions: (1) where classical HP plot is fully valid, typically over 30 nm, (2) where a departure from HP is first noticed, typically below 30nm and (3) where HP plot starts to fall drastically, typically below 15 nm (for details see reference [9]). As the average grain size in nanomaterial is lowered say below 10nm, the dislocations inside most likely do not exist, and there are probably no FR or GB sources operating. Although GB can still be a source of partial dislocations. We will consider this in next section.

5.2. Dislocation Emission from Grain Size Less than 20nm

By now, extensive experiments and simulations exist to show the important role that stress-assisted nanograin rotation play in GB-mediated deformation mode in NC materials. In fact, it is clear that the rotation of nanograins has a close correlation with the enhanced dislocation activity and plasticity in NC metals and alloys.

Li et al. [48] propose a theoretical model to investigate the dislocation emission behavior in NC face-centered cubic crystals. Noting that the nanograin rotation dominates the deformation in these materials, they investigate energy characteristics and the critical shear stress that is required to trigger the dislocation emission from GBs. Their important results show that the "nanograin rotation process can make the originally energetically unfavorable dislocation emission process favorable". They show that the critical stress can also be extraordinarily reduced as compared with the rotation-free case. For example, the proposed dislocation emission process can reduce the required external stress to almost zero if the rotation magnitude can reach 8.5 and 2.9 degrees for Al and Pt, respectively. The findings thus establish that nanograin rotation is a very effective dislocation-emission mechanism in NC materials. Thus, it possibly explains the experimentally observed rotation-dislocation correlation in NC materials. For example, Wang et al. [49] experimentally investigated the atomic-scale deformation dynamic behaviors of Pt nanocrystals with size of ∼18 nm in situ. They used a homemade device in a high-resolution TEM for this purpose. They found that the plastic deformation of the nanosized single crystalline Pt commenced first with dislocation "appearance" then followed by a dislocation "saturation" phenomenon. It was also clear that the magnitude of strain plays a key role on dislocation behaviors in these materials. More recently, these results were confirmed by extensive experiments and molecular dynamics simulations by Liu et al. [50]. They also find that stress-driven grain growth can greatly contribute to enhanced dislocation emission and tensile ductility in NC metals. What is the underlying mechanism behind this correlation? Liu et al. [50] propose a theoretical model based on the cooperative nanograin rotation and GB migration for grain growth to explain the enhanced dislocation emission from GBs.

One should also note the important results obtained by Swygenhoven and Derlet. They investigated [51], GB sliding using MD computer simulations. They used a model of Ni NC sample with a mean grain size of 12 nm under uniaxial tension. They found atomic shuffling and stress-assisted free-volume migration. The activated accommodation

processes under high-stress and room temperature conditions are shown to be GB and triple-junction migration, and dislocation activity.

From these studies, it becomes abundantly clear that GB dislocations in GB and their emission plays a very significant role sliding or rotation of the GB. The sliding or rotation are necessary to explain the deformation behavior and dislocation emission of grains about 15 nm or less in NC materials.

6. Summary

We have showed the importance of the mechanism of emission of dislocations from GBs, especially in case of NC materials where FR dislocation sources are difficult to operate. We also briefly mentioned the direct observation of GB dislocation mechanism by experimental methods. Of course, in even finer grains, dislocations have no role to play, except at the GBs. Therefore, although it appears that the dislocation pile-up model is still the most frequently favored model to explain the HP relationship, the other models have their own merit and advantages. It is especially clear that the Li mechanism plays an important role in the deformation studies of many types of materials, especially in nanomaterials. Furthermore, one should note that the HP relationships applies not only to yield stress, but also to flow and fracture stresses and even to fatigue and creep. Thus, it appears that the HP type size dependence of strength is a rather general result of natural dislocation behavior. Revealing various aspects of physics behind the HP law, especially in nanomaterials, remains an attractive and challenging type of research.

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