Special strain hardening mechanism and nanocrack generation in nanocrystalline materials

I. A. Ovid'ko[a] and A. G. Sheinerman[b]
Institute for Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vas. Ostrov, St. Petersburg 199178, Russia

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A special mechanism of strain hardening in deformed nanocrystalline materials (NCMs) is suggested and theoretically described. The mechanism represents generation of disclination dipoles at grain boundaries (GBs) due to GB sliding. It is shown that special strain hardening can effectively suppress plastic flow instability in metallic and ceramic NCMs and thus enhance their ductility. At the same time, the disclination dipoles formed due to GB sliding serve as dangerous stress sources that can induce nucleation of nanocracks, decreasing ductility of NCMs. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734393]

Metallic and ceramic nanocrystalline materials (NCMs) are commonly characterized by very high values of strength and hardness which are attractive for diverse technological applications.[1–3] At the same time, utilization of high-strength NCMs is impeded by their low tensile ductility. In most cases, low tensile ductility is related to plastic strain instability—dramatic plastic flow localization followed by failure—in NCMs where plastic deformation is specified by weak strengthening or its absence.[4–7] This behavior is contrasted to that of ductile coarse-grained polycrystals deformed through the slip of conventional lattice dislocations whose storage provides pronounced strain hardening, the key factor suppressing plastic strain instability. The absence of strengthening in NCMs is attributed to the action of specific deformation mechanisms [grain boundary (GB) sliding, twin deformation, rotational deformation, etc.] that operate in these materials at very high stresses.[8–17] The action of such high stresses also can cause crack nucleation and growth instability, decreasing ductility of NCMs.[5,18,19] Recently, however, several examples of good tensile ductility and even superplasticity of superstrong NCMs have been reported.[20–25] The nature of unique combination of ultrahigh strength and good ductility of these materials is not understood. The main aim of this letter is to suggest and theoretically describe a special mechanism for strain hardening that can suppress plastic strain instability in deformed NCMs. The mechanism represents the generation of disclination dipoles at GBs due to GB sliding. Also, we estimate the conditions for nanocrack formation in the stress field of such disclination dipoles.

Plastic flow in NCMs—aggregates of nanoscale grains with various crystal lattice orientations—is commonly accompanied by relative displacements of grains and corresponding movement of triple junctions of GBs. In particular, such processes accompany GB sliding that often essentially contributes to plastic flow of NCMs. In the limiting cases of superplastic and high-strain deformation regimes, cooperative GB sliding occurs along the mesoscopic sliding surfaces—chains of GBs with approximately parallel planes—in NCMs (Refs. 24–26) [Fig. 1(a)]. In general, both cooperative GB sliding at mesoscopic sliding surfaces [Fig. 1(a)] and "conventional" GB sliding along curved GBs result in significant relative displacements of grains and corresponding movement of triple junctions in NCMs. At the same time, for geometric reasons, such displacements and movement lead to the formation of GB disclinations—defects of rotational type—that can cause strain hardening in NCMs.

Let us consider the formation of GB disclinations in the exemplary case of GB sliding at mesoscopic sliding surfaces in NCMs. For simplicity, we will focus our consideration on a model arrangement of rectangular grains with a triple junction of GBs, including a vertical GB characterized by the tilt misorientation parameter ω, see Fig. 1(b). The horizontal GBs shown in Fig. 1(b) are supposed to belong to a mesoscopic sliding surface and thereby to conduct intensive GB

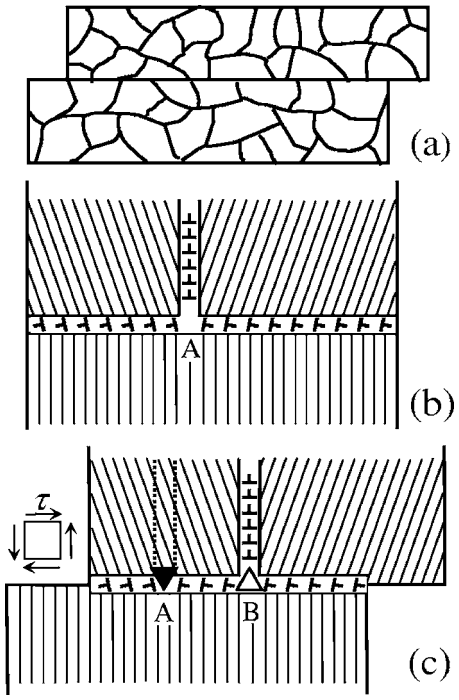

FIG. 1. Grain boundary sliding along a mesoscopic sliding surface in a nanocrystalline material. (a) General schematic view. [(b) and (c)] A large-view illustration of formation of a disclination dipole due to grain boundary sliding along a mesoscopic sliding surface (schematically): (b) initial and (c) final states. (For simplicity, crystal lattice distortions created by the disclination dipole are not shown.)

[a]Electronic mail: ovidko@def.ipme.ru
[b]Electronic mail: shein77@mail.ru

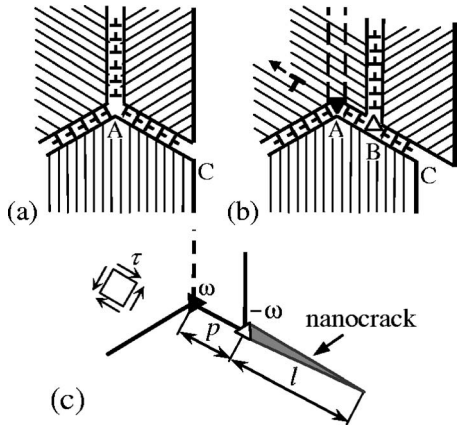

FIG. 2. Formation of a disclination dipole and nanocrack due to conventional grain boundary sliding in a nanocrystalline material (schematically). (a) Initial state. (b) A disclination dipole is formed due to sliding along the grain boundary AC. (For simplicity, crystal lattice distortions created by the disclination dipole are not shown.) Grain boundary sliding is accommodated by emission of lattice dislocations into the left upper grain. (c) A nanocrack nucleates at a disclination dipole.

sliding under an external shear stress τ. GB sliding gives rise to movement of the triple junction from its initial position A to a new position B [Fig. 1(c)]. In the initial state [Fig. 1(b)], the GBs that form the triple junction A are supposed to be geometrically compensated. There is no angle gap at this triple junction or, in other words, the sum of GB misorientation angles at the junction is equal to zero. When the triple junction is shifted by GB sliding from its initial position A to another position B [Fig. 1(c)], the angle gaps $-\omega$ and ω appear at GB junctions A and B, respectively. In the theory of defects in solids, junctions A and B with the angle gaps $\pm\omega$ are considered as partial wedge disclinations (rotational defects) with the strengths $\pm\omega$.[3,27] Similar disclination defects were experimentally observed in iron under ball-mill treatment resulting in the nanostructure formation.[28]

Also, GB disclinations form in NCMs deformed by conventional GB sliding along curved GBs. This is illustrated in Figs. 2(a) and 2(b) showing GB sliding along a GB AC that results in the displacement of the triple junction (from position A to position B) and is accommodated by emission of lattice dislocations into the left upper grain. For the same geometric reasons as with GB sliding at mesoscopic sliding surfaces (Fig. 1), partial wedge disclinations form at GB junctions A and B [Fig. 2(b)]. The disclinations at junctions A and B form a dipole configuration and are attracted to each other. As GB sliding proceeds, the distance AB between the disclinations increases. This results in an increase of the external shear stress necessary to surmount disclination attraction and provide plastic flow along GBs.

Let us estimate the effect of disclinations on strain hardening in NCMs. To do so, we consider a model nanocrystalline solid that has a mean grain size d and is deformed by conventional GB sliding accommodated by lattice dislocation slip [Fig. 2(b)]. In a first approximation, we assume that essential GB sliding is carried only by favorably oriented GBs whose planes make small angles with the directions of the maximum shear stress. GB sliding is characterized by the macroscopic plastic strain $\varepsilon \approx \alpha p/d$, where p is the mean value of triple junction translation produced by GB sliding and α (<1) is the fraction of GBs that carry GB sliding.

Let us estimate the energy change ΔW of the nanocrystalline specimen due to GB sliding. In a first approximation, the energy change ΔW (per unit area of specimen sections parallel to the directions of the maximum shear stress) can be estimated as

$$\Delta W = \frac{D\omega_0^2 p^2}{2d}\left\{\ln\frac{R}{p}+\frac{1}{2}\right\}+(\tau_0-\tau)p, \tag{1}$$

where ω_0 is the mean absolute value of the disclination strength, R is the screening length of the disclination dipole stress field, τ_0 is the internal stress that characterizes resistance to GB sliding in the absence of the disclination dipoles, $D=G/[2\pi(1-\nu)]$, G is the shear modulus, and ν is Poisson's ratio. The first and second terms on the right-hand side of formula (1) characterize the self-energy of the disclination array and the opposite of the work of the shear stress τ spent to GB sliding, respectively. In doing so, the self-energy of the disclination array is roughly estimated as the sum of the self-energies of individual disclination dipoles, using the methods of the disclination theory.[27] The interaction between different disclination dipoles leads to the mutual screening of their stress fields. This effect is characterized by assigning a screening length R to the stresses of the disclination dipoles.

Plastic flow is energetically favorable if $\partial\Delta W/\partial p<0$ and unfavorable otherwise. In the case of a quasiequilibrium plastic deformation, we have $\partial\Delta W/\partial p=0$. With formula (1) and the expression $p=\varepsilon d/\alpha$, the latter equality yields the following expression for the disclination-induced contribution τ_d to the global flow stress:

$$\tau_d = \frac{D\omega_0^2\varepsilon}{\alpha}\ln\frac{\alpha R}{\varepsilon d}. \tag{2}$$

According to formula (2), τ_d increases with rising ε, if $\varepsilon<\alpha R/(ed)$ (where $e\approx 2.718$). Formula (2) describes special strain hardening due to the formation of GB disclinations. This hardening is inherent to NCMs where the amounts of GBs and their triple junctions are very large.

Let us estimate the characteristic values of τ_d, for nanocrystalline Cu (having the shear modulus $G=48$ GPa and Poisson's ratio $\nu=0.34$), Ni (with $G=73$ GPa and $\nu=0.34$), and Al_2O_3 (with $G=150$ GPa and $\nu=0.25$). For definiteness, the characteristics of the defect configuration under consideration are taken as $R=3d$, $d=50$ nm, $\alpha=1/3$, and $\omega_0=\pi/9$ ($=20°$). With these characteristics and formula (2), in the case of nanocrystalline Cu, we obtain $\tau_d\approx 0.2$ GPa at $\varepsilon=0.01$. For Ni, we find $\tau_d\approx 0.5$ and 0.68 GPa at $\varepsilon=0.02$ and 0.03, respectively. With the same characteristics, in the case of nanocrystalline Al_2O_3, formula (2) yields $\tau_d\approx 0.91$ and 1.22 GPa at $\varepsilon=0.02$ and 0.03, respectively. Thus, even for low plastic strain, the formation of GB disclinations causes pronounced strain hardening in NCMs and thereby can suppress plastic strain instability.

At the same time, the disclinations produced by GB sliding serve as powerful stress sources that can induce the nucleation of nanocracks, decreasing ductility of NCMs. Let us consider the model situation where a nanocrack nucleates in the stress field of a dipole of disclinations with the strengths $\pm\omega$ formed due to GB sliding. The nanocrack is assumed to have a length l and nucleate at the disclination with the strength $-\omega$, along a GB in the region where the tensile stresses exerted on the crack surfaces by the disclination dipole are highest [see Fig. 2(c)].

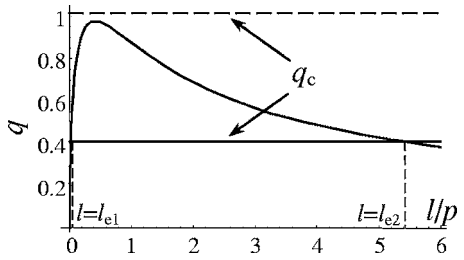

FIG. 3. Dependence of the parameter q on the normalized nanocrack length l/p, for Ni (see text). The solid and dashed horizontal lines show the values of the parameter q_c for $p=5$ nm and $p=2$ nm, respectively.

To calculate the conditions for nanocrack growth, we use the energetic criterion[29,30] suggesting that a crack is favored to grow if the release of the strain energy in the course of crack advance is larger than the effective surface energy of the crack surfaces. With this criterion, after some algebra, we find the following condition of energetically favorable nanocrack growth: $q(\tilde{l})>q_c$, where $\tilde{l}=l/p$,

$$q(\tilde{l})=\tilde{l}\left[\left(\frac{2(\sqrt{1+\tilde{l}}-1)}{\tilde{l}}-\ln\frac{\sqrt{1+\tilde{l}}+1}{\sqrt{1+\tilde{l}}-1}\right)^2+\left(\frac{\tau}{D\omega}\right)^2\right], \tag{3}$$

$q_c=16\pi(1-\nu)(2\gamma-\gamma_b)/[Gp\omega^2]$, γ is the specific surface energy, and γ_b is the specific GB energy (released during nanocrack growth along a GB).

With the above formulas, we calculated both q_c and the dependence $q(\tilde{l})$ (see Fig. 3) in the exemplary case of $\tau=0.7$ GPa, $\omega=\pi/4$, and the following parameters of nanocrystalline Ni: $G=73$ GPa, $\nu=0.34$, $\gamma=1.725$ J/m^2, and $\gamma_b=0.69$ J/m^2. In this case, the dependence $q(\tilde{l})$ first increases and then decreases with rising $\tilde{l}$. Analysis of the criterion $q(\tilde{l})>q_c$ shows that the formation of a nanocrack is not likely, if the values of the disclination strength ω and/or disclination dipole arm p are not too large. In contrast, for large enough values of ω and/or p, nanocrack growth is energetically favored when its length l lies in an interval $l_{e1}<l<l_{e2}$, where the critical lengths l_{e1} and l_{e2} are determined by the equation: $q(\tilde{l})=q_c$. Nanocrack nucleation and growth in the range $l<l_{e1}$ require thermal fluctuations. Its subsequent growth within the length range $l_{e1}<l<l_{e2}$ occurs athermally. Further nanocrack growth is energetically forbidden. For instance, following our calculations in the case of Ni, for $\omega=\pi/4$, $p=5$ nm, and $d=50$ nm, we have $l_{e2}\approx 5p=d/2$. That is, the equilibrium nanocrack length l_{e2} is around half of the grain size d or more. The formation and convergence of such nanocracks can provide the experimentally observed[18,19] brittle intergranular fracture of NCMs.

A similar analysis of nanocrack generation at disclination dipoles formed due to GB sliding in nanocrystalline Cu has demonstrated that, in contrast to Ni, due to lower flow stresses and shear modulus, the formation of nanocracks at disclination dipoles in Cu is favorable only at very large values of ω. For instance, the nanocracks with the length of several nanometers can nucleate at disclination dipoles with $\omega\approx\pi/3$ or more.

Thus, wedge disclinations are produced by GB sliding in metallic and ceramic NCMs and serve as powerful stress sources. The disclinations cause competing effects on ductility of NCMs. First, the formation of disclinations provides strain hardening (that suppresses plastic strain instability) in deformed NCMs and thereby enhances their ductility. Second, the disclinations initiate the nucleation and growth of nanocracks in deformed NCMs and thereby decrease their ductility. In this context, NCMs can show experimentally observed[20–25] good ductility or even superplasticity, if disclination formation is accompanied by intensive relaxation processes—diffusion and lattice dislocation emission from GBs—releasing in part the disclination stresses. In this case, disclination formation causes moderate strain hardening that both suppresses plastic strain instability and does not initiate crack nucleation.

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