
Volume 60, issue 1, January 2009
ISSN 1359-6462
ELSEVIER
Scripta MATERIALIA
A LETTERS JOURNAL
STRUCTURE
PROPERTIES
THEORY
PROCESSING
FUNCTION
Available online at ScienceDirect www.sciencedirect.com
www.elsevier.com/locate/scriptamat

Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 60 (2009) 36–39
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Emission of partial dislocations from amorphous intergranular boundaries in deformed nanocrystalline ceramics

S.V. Bobylev,[a] A.K. Mukherjee[b] and I.A. Ovid'ko[a,*]

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

[b]*University of California, Davis, 1 Shields Avenue, Davis, CA 95616, USA*

Received 7 August 2008; revised 21 August 2008; accepted 24 August 2008
Available online 9 September 2008

A theoretical model is suggested that describes emission of partial lattice dislocations from amorphous intergranular boundaries into crystalline grains in deformed nanocrystalline ceramics. Within the model, a dipole of immobile lattice dislocations is generated at an amorphous intergranular boundary through local shear events in this boundary. One of the dislocations then undergoes transformation, resulting in emission of a partial dislocation into a grain. It is shown that the emission process is energetically favorable in nanoceramic SiC deformed at high stresses.

Keywords: Dislocations; Ceramics; Nanocrystalline materials

Nanocrystalline (nc) ceramic bulk materials, coatings and films show outstanding mechanical properties such as superstrength, superhardness and high wear resistance [1–12]. The deformation behavior of nc ceramics is strongly influenced by intergranular boundaries which often have an amorphous structure and occupy very large volume fractions in nc specimens—see, e.g., experimental data [12–14] and computer simulations [15,16]. For instance, following computer simulations [15], there is a crossover from intergranular plastic deformation to intragranular lattice slip in the nc cubic phase of silicon carbide (3C-SiC) under indenter load. At the first stage of indenter load, plastic deformation occurs in amorphous intergranular boundaries (AIBs), while the crossover to partial dislocation slip in nanoscale grains is realized at the latter stage of indenter load. In doing so, in simulations [15], partial dislocations in grains were observed to be emitted from AIBs connected by stacking faults. Computer simulations [17] have shown similar partial dislocations emitted from amorphous layers in metallic crystal–glass nanolaminates. In addition, the joining of stacking faults to opposite amorphous layers was experimentally observed in metallic crystal–glass nanolaminates after plastic deformation [17]. In this context, since the activity of conventional dislocation sources (like Frank–Read ones) is suppressed in nanoscale grains [12,18], AIBs are expected to be sources that emit lattice dislocations in deformed nc ceramics. However, a micromechanism of dislocation emission from AIBs is unclear (in contrast to conventional grain boundaries that emit lattice dislocations due to transformations of pre-existing grain boundary dislocations [19–21]). At the same time, knowledge on such a micromechanism is of primary importance for understanding the fundamentals of both plastic flow and its transfer from the amorphous phase to adjacent crystallites in nc ceramics. The main aim of this paper is to suggest a theoretical model describing emission of partial dislocations from AIBs in deformed nc ceramics.

Let us consider an nc ceramic solid consisting of nanoscale grains divided by AIBs. A typical fragment of the solid and its evolution under mechanical load are schematically shown in Figure 1. Within our model, when mechanical load is applied to the solid, plastic shear initially occurs in AIB planes where the maximum shear stress operates. In particular, the plastic shear occurs in the horizontal AIB strip shown in Figure 1. Following the concept [22–24] on local shear events—shear transformations of local atomic clusters—as carriers of plastic flow in amorphous solids, we suppose that the plastic shear is carried by local shear events occurring within the horizontal AIB (Fig. 1b and c). In doing so,

* Corresponding author. Tel.: +7 812 321 4764; fax: +7 812 321 4771; e-mail: ovidko@def.ipme.ru

1359-6462/$ - see front matter © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2008.08.025

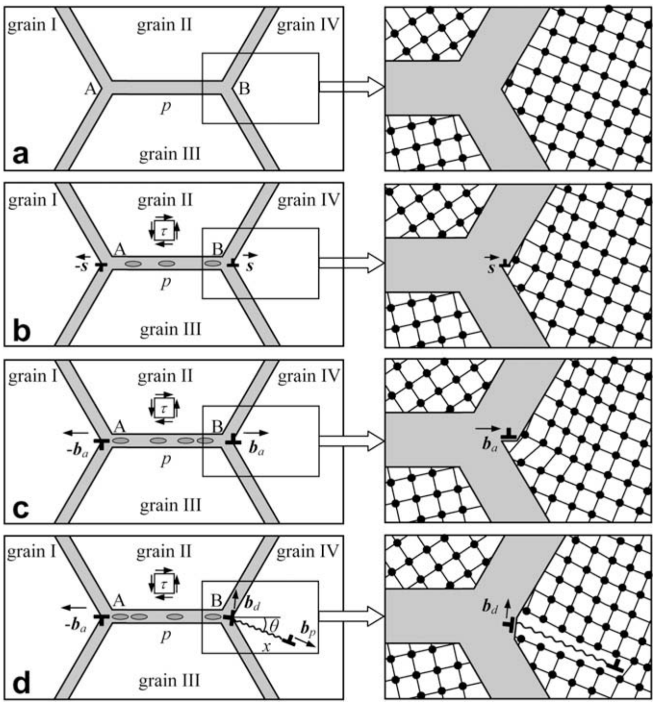

Figure 1. Generation of dislocation dipole at an amorphous intergranular boundary is followed by emission of a partial dislocation into an adjacent crystalline grain in a deformed nc ceramic specimen (schematically). (a) Initial, dislocation-free state. Four grains I, II, III and IV are divided by amorphous intergranular boundaries (grey strips). (b) Generation of a dipole of edge dislocations with Burgers vectors $\pm\boldsymbol{s}$ at crystal–glass interfaces A and B due to local shear events (ellipses) within the boundary region. (c) Further plastic shear in the amorphous boundary region results in increase of dislocation Burgers vectors up to $\pm\boldsymbol{b}_a$. (d) Splitting of one of the dislocations of the dipole results in formation of both a residual immobile dislocation and a mobile partial dislocation that glides in grain IV. The glide of the partial dislocation is accompanied by formation of stacking fault (wavy line). Magnified insets (a)–(d) illustrate evolution of the dislocation structure at the crystal–glass interface B.

the magnitude of the shear gradually increases in parallel with the number of the local shear events.

Note that the plastic shear occurs in the plane AIB of finite length p. In this case, according to the theory of dislocations in continuum media [25,26], edge dislocations are generated as line defects that bound a finite plane region where the plastic shear occurs. More precisely, the dislocations are generated at opposite interfaces A and B between the amorphous boundary strip and the adjacent grains I and IV, respectively, as shown in Figure 1a–c. The dislocations form a dipole. The Burgers vectors of the dislocations are defined by the magnitude and direction of the plastic shear within the AIB. Since the magnitude of the plastic shear gradually increases in parallel with the number of local shear events occurring in the AIB under the action of the shear stress τ, the Burgers vector magnitude s of the dislocations of the dipole gradually grows from 0 (Fig. 1a) to some value b_a (Fig. 1c). In general, the Burgers vectors $\boldsymbol{b}_a$ and $-\boldsymbol{b}_a$ of the dislocations are not lattice vectors, because the dislocations result from gradual accumulation of local shear events within the AIB. At the same time, in terms of Volterra's definition [25,26] of dislocations in continuum media, $\boldsymbol{b}_a$ and $-\boldsymbol{b}_a$ are defined as the dislocation Burgers vectors.

The dislocations of the dipole are located at the interfaces, A and B, between the amorphous and crystalline phases, in which case they can undergo dislocation reactions producing mobile lattice dislocations. In particular, each of such dislocations can split into a mobile lattice (partial or perfect) dislocation that glides in the adjacent grain and a residual immobile dislocation that stays at the AIB (Fig. 1d). Below, we will consider the case of partial mobile dislocations (Fig. 1d), because computer simulations [15] show partial dislocations emitted from AIBs in nc ceramics.

In accordance with the suggested model of dislocation emission from AIBs (Fig. 1), this process can be divided into the two stages: (i) generation of a dislocation dipole at the AIB (Fig. 1a–c) and (ii) the dislocation splitting transformation that results in emission of a partial dislocation from the AIB (Fig. 1d). Let us calculate both the energy characteristics and critical stresses needed for athermal realization of the two stages. In doing so, after some algebra based on the theory of dislocations, we find the following expression for the energy change ΔW_1 characterizing stage (i):

$$\Delta W_1 = Ds^2\left(\ln\frac{p-s}{s}+1\right) - (\tau-\tau_a)sp, \tag{1}$$

where $D = G/[2\pi(1 - \nu)]$, G is the shear modulus, ν is the Poisson ratio, $s(0 \leqslant s \leqslant b_a)$ is the Burgers vector magnitude of the dislocations (Fig. 1b and c), p denotes the length of the AIB, τ is the shear stress acting in the AIB plane, and τ_a is the stress characterizing the resistance of the amorphous phase to plastic shear. The first term on the right-hand side of Eq. (1) describes the elastic energy of the dislocation dipole, and the second term represents the work of the shear stress, which is spent generating the dislocation dipole.

When the Burgers vector magnitude reaches some critical value $\boldsymbol{b}_a$, stage (ii) occurs. That is, one of the dislocations splits into an immobile edge dislocation and a mobile partial edge dislocation (Fig. 1d). The mobile dislocation has the Burgers vector $\boldsymbol{b}_p$ and glides along the crystal slip plane tilted by angle θ relative to the plane AB (Fig. 1d). The residual dislocation stays at the crystal–glass interface B and has the Burgers vector $\boldsymbol{b}_d = \boldsymbol{b}_a - \boldsymbol{b}_p$ with magnitude $b_d = \sqrt{b_a^2 + b_p^2 - 2b_a b_p \cos\theta}$.

Also, after some algebra based on the theory of dislocations, we found the energy change ΔW_2 characterizing stage (ii). It is given as:

$$\Delta W_2 = Db_p\left\{b_p\left(\ln\frac{x-b_p}{b_p}+1\right)+b_a\left[\cos\theta\left(\ln\frac{Lb_p}{px}-1\right)-\frac{px\sin^2\theta}{L^2}\right]\right\}+\gamma x-(\tau-\tau_p)b_p x\cos 2\theta. \quad (2)$$

Here x is the distance moved by the emitted partial dislocation, $L = \sqrt{p^2 + x^2 + 2px\cos\theta}$, γ is the stacking fault energy (per unit area), and τ_P denotes the Peierls stress characterizing the resistance of the crystal lattice to the dislocation glide. The first term on the right-hand side of formula (2) describes the elastic energy of the dislocations, the second term characterizes the stacking fault energy, and the third term is the work of the shear stress, spent on gliding of the mobile dislocation.

Let us define the first critical stress $\tau = \tau_{c1}$ as the minimum stress at which curve $\Delta W_1(s)$ monotonously decreases with increasing s from 0 to b_a. This stress is given analytically by the following combination of the conditions:

$$\begin{cases} \Delta W_1(s) < 0, & \text{if } s > 0 \\ \frac{\partial \Delta W_1}{\partial s} = 0, & \text{if } s = b_a. \end{cases} \quad (3)$$

With formula (1), the conditions (3) include the flow stress τ_a of the amorphous phase. In general, τ_a is highly sensitive to both temperature and strain rate. For low temperatures and/or high strain rates, athermal plastic deformation occurs. Following experiments [27], the microhardness H_V of amorphous SiC is around 30 GPa. This value of H_V, according to the standard relation $\tau_f \approx H_V/6$ between H_V and athermal flow stress τ_f [28], corresponds to the athermal flow stress $\tau_a = 5$ GPa of amorphous SiC. The stress level significantly decreases with rising temperature and/or decreasing strain rate, in which case thermally assisted deformation occurs. In this case, for definiteness, we will take $\tau_a = 1$ GPa. For typical parameters ($G = 217$ GPa, $\nu = 0.23$ [29], $p = 10$–50 nm, $\tau_a = 1$–5 GPa) of nc 3C-SiC, the first inequality in formula (3) is always valid, if the second condition is valid. The second condition causes the following expression for the first critical stress τ_{c1}:

$$\tau_{c1} = \tau_a + \frac{Db_a}{p}\left(\ln\frac{p-b_a}{b_a}+\frac{1}{2}\frac{p-2b_a}{p-b_a}\right). \quad (4)$$

Let us define the second critical stress τ_{c2} as the minimum stress at which curve $\Delta W_2(x)$ monotonously decreases with rising x. That is, emission of a partial dislocation (Figure 1d) is energetically favorable and occurs without any energy barrier, when $\tau \geqslant \tau_{c2}$. The stress τ_{c2} is given analytically by the following combination of the conditions for $\Delta W_2(x)$ at point $x = b_a + b_p$:

$$\begin{cases} \Delta W_2(x = b_a + b_p) \leqslant 0, \\ \left.\frac{\partial \Delta W_2}{\partial x}\right|_{x=b_a+b_p} \leqslant 0. \end{cases} \quad (5)$$

Each of the conditions (5) defines its critical value of the stress. The first condition results in the following critical value:

$$\tau'_{c2} = \tau_p + \frac{D}{x_0\cos 2\theta}\left\{b_p\left(\ln\frac{b_a}{b_p}+1\right)+b_a\left[\cos\theta\left(\ln\frac{L_0 b_p}{px_0}-1\right)-\frac{px_0\sin^2\theta}{L_0^2}\right]\right\}+\frac{\gamma}{b_p\cos 2\theta}. \quad (6)$$

Here $x_0 = b_a + b_p$, $L_0 = \sqrt{p^2 + x_0^2 + 2px_0\cos\theta}$. The second condition in formula (5) results in the following critical value:

$$\tau''_{c2} = \tau_p + \frac{D}{\cos 2\theta}\left\{\frac{b_p}{x_0}-\frac{b_a p}{L_0^2}\left[\frac{\cos\theta(p + x_0\cos\theta)}{x_0}+\frac{(p^2-x_0^2)\sin^2\theta}{L_0^2}\right]\right\}+\frac{\gamma}{b_p\cos 2\theta}. \quad (7)$$

The critical stress τ_{c2} represents the largest value of the stresses given by formulas (6) and (7): $\tau_{c2} = \max\{\tau'_{c2}, \tau''_{c2}\}$. With this expression and formulas (4), (6), and (7), we calculated τ_{c2}, for typical values of parameters of nc 3C-SiC ($G = 217$ GPa, $\nu = 0.23$ [29], $p = 10$–50 nm, the lattice parameter $a = 4.36$ Å [30], the Burgers vector magnitude $b_p = a/\sqrt{6} = 1.78$ Å for Shockley partial dislocations, the stacking fault energy $\gamma = 0.1$ mJ m^{-2} [31], and the Peierls stress $\tau_P \approx 7.5$ GPa [32]). According to our calculations, in most cases (except for the case of $p \leqslant 10$ nm), one has $\tau_{c1} < \tau_{c2}$, when s grows from 0 to some value b_a^*. In these cases, plastic flow in nc 3C-SiC starts to occur in AIBs and then, with increase in the applied stress, transfers to crystalline grains. Such deformation behavior was observed in simulations [15] of indenter load of nc 3C-SiC.

The expressions $\tau_{c2} = \max\{\tau'_{c2}, \tau''_{c2}\}$, $\tau_{c1}(b_a) = \tau_{c2}(b_a)$ and formulas (4), (6), and (7) define the critical stress τ_c needed to cause the dislocation emission from AIBs or, in other words, the crossover from intergranular plastic flow to intragranular lattice slip. More precisely, τ_c is found as follows. For given values of p and θ, we numerically find the solution of the equation $\tau_{c1}(b_a) = \tau_{c2}(b_a)$. The solution is the Burgers vector magnitude b_a^*, at which $\tau_{c1} = \tau_{c2}$. Then we have the critical stress $\tau_c = \tau_{c1}(b_a^*) = \tau_{c2}(b_a^*)$. The dependence $\tau_c(p)$ at an example value of $\theta = 20°$ is shown in Figure 2, for $\tau_a = 1$ and 5 GPa (solid and dashed curves, respectively). For $\tau_a = 1$ GPa, the critical stress τ_c ranges from 5 to 9 GPa, depending on p. This stress level is typical for nc 3C-SiC under indenter load. For instance, following experiments [33], the microhardness H_V of nc SiC ranges from 30 to 50 GPa. These values of H_V, according to the standard relation

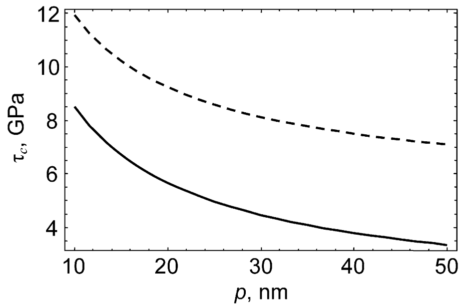

Figure 2. Dependence of the critical shear stress τ_c (at which crossover from intergranular plastic flow in amorphous boundaries to intragranular lattice slip grains occurs) on amorphous boundary length (grain size) p, for $\theta = 20°$, and $\tau_a = 1$ and 5 GPa (solid and dashed curves, respectively).

$\tau_f \approx H_V/6$ [28], correspond to the stresses $\tau_f \approx 5$–8 GPa.

For $\tau_a = 5$ GPa, the critical stress τ_c (dashed curve in Fig. 2) ranges from 8 to 12 GPa, depending on p. This stress level is high. However, it can also be reached locally in deformed nc 3C-SiC. In particular, computer simulations [15] have shown shear stresses of $\approx$18 GPa in some local regions of nc SiC under indenter load.

In summary, we have proposed a theoretical model to describe the emission of lattice dislocations from AIBs in deformed nc ceramics. It has been shown that the emission process is energetically favorable and can occur in athermal way (without any energy barrier) in nc 3C-SiC. The critical shear stress τ_c needed to cause the athermal emission decreases with increasing AIB length p (or, in other terms, grain size). In these circumstances, crossover from intergranular plastic flow in AIBs to intragranular lattice slip in nc ceramics is expected to be hampered by decreasing grain size.

The work was supported, in part, by the the National Science Foundation Grant CMMI #0700272, the Office of US Naval Research (Grant No. N00014-08-1-0405), Russian Academy of Sciences Program "Structural Mechanics of Materials and Construction Elements", and the Russian Foundation of Basic Research (Grant No. 08-01-00225-a).

[1] R.W. Siegel, S.K. Chang, B.J. Ash, J. Stone, P.M. Ajayan, R.W. Doremus, L.S. Schadler, Scr. Mater. 44 (2001) 2061.
[2] G.-D. Zhan, J.D. Kuntz, J. Wan, J. Garay, A.K. Mukherjee, Scr. Mater. 47 (2002) 737.
[3] G.-D. Zhan, J.D. Kuntz, J. Wan, A.K. Mukherjee, Nat. Mater. 2 (2002) 38.
[4] S. Veprek, Rev. Adv. Mater. Sci. 5 (2003) 6.
[5] D. Galvan, Y.T. Pei, J.Th.M. De Hosson, Surf. Coat. Technol. 200 (2005) 6718.
[6] G.-D. Zhan, A.K. Mukherjee, Rev. Adv. Mater. Sci. 10 (2005) 185.
[7] D. Galvan, Y.T. Pei, J. Th.M. De Hosson, Acta Mater. 53 (2005) 3925.
[8] Y.T. Pei, D. Galvan, J.Th.M. De Hosson, Acta Mater. 53 (2005) 4505.
[9] Y.T. Pei, D. Galvan, J.Th.M. De Hosson, C. Strondl, J. Eur. Ceram. Soc. 26 (2006) 565.
[10] K. Chihara, D. Hiratsuka, J. Tatami, F. Wakai, K. Komeya, Scr. Mater. 56 (2007) 871.
[11] J. Lian, J.E. Garay, J. Wang, Scr. Mater. 56 (2007) 1095.
[12] C.C. Koch, I.A. Ovid'ko, S. Seal, S. Veprek, Structural Nanocrystalline Materials: Fundamentals and Applications, Cambridge University Press, Cambridge, 2007.
[13] X. Zhou, D.M. Hulbert, J.D. Kunz, R.K. Sadangi, V. Shukla, B. Kear, A.K. Mukherjee, Mater. Sci. Eng. A 394 (2005) 353.
[14] X. Xu, T. Nishimura, N. Hirosaki, R.-J. Xie, Y. Yamamoto, H. Tanaka, Acta Mater. 54 (2006) 255.
[15] I. Szlufarska, A. Nakano, P. Vashista, Science 309 (2005) 911.
[16] Y. Mo, I. Szlufarska, Appl. Phys. Lett. 90 (2007) 181926.
[17] Y. Wang, J. Li, A.V. Hamza, T.W. Barbee Jr., Proc. Natl. Acad. Sci. USA 104 (2007) 11155.
[18] J. Weissmueller, J. Markmann, Adv. Eng. Mater. 7 (2005) 202.
[19] X.Z. Liao, F. Zhou, E.J. Lavernia, S.G. Srinivasan, M.I. Baskes, D.W. He, Y.T. Zhu, Appl. Phys. Lett. 83 (2003) 632.
[20] A.G. Froseth, P.M. Derlet, H. Van Swygenhoven, Acta Mater. 52 (2004) 5863.
[21] S.V. Bobylev, M.Yu. Gutkin, I.A. Ovid'ko, Acta Mater. 52 (2004) 3793.
[22] A.S. Argon, Acta Metall. 27 (1979) 47.
[23] M.J. Demkowicz, A.S. Argon, Phys. Rev. B 72 (2005) 245205.
[24] M.J. Demkowicz, A.S. Argon, Phys. Rev. B 72 (2005) 245206.
[25] V. Volterra, Ann. Ecole Normale Sup. Paris 24 (1907) 401.
[26] J.P. Hirth, J. Lothe, Theory of Dislocations, Wiley, New York, 1982.
[27] M.A.E. Khakani, M. Chaker, A. Jean, S. Boily, J.C. Kieffer, M.E. O'Hern, M.F. Ravet, F. Rousseaux, J. Mater. Res. 9 (1994) 96.
[28] S. Veprek, S. Mukherjee, P. Karvankova, H.-D. Mannling, J.L. He, K. Moto, J. Prochazka, A.S. Argon, J. Vac. Sci. Technol. A 21 (2003) 532.
[29] Z. Ding, S. Zhou, Y. Zhao, Phys. Rev. B 70 (2004) 184117.
[30] J. Kräußlich, A.J. Bauer, B. Wunderlich, K. Goetz, Mater. Sci. Forum 353–356 (2001) 319.
[31] U. Kaiser, I.I. Khodos, Philos. Mag. A 82 (2002) 541.
[32] H.-P. Chen, R.K. Kalia, A. Nakano, P. Vashishta, I. Szlufarska, J. Appl. Phys. 102 (2007) 063514.
[33] F. Liao, S.L. Girshick, W.M. Mook, W.W. Gerberich, M.R. Zachariah, Appl. Phys. Lett. 86 (2005) 171913.