

# Special rotational deformation in nanocrystalline metals and ceramics

I.A. Ovid'ko\* and A.G. Sheinerman

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

Received 5 February 2008; revised 26 February 2008; accepted 26 February 2008  
Available online 10 March 2008

A model is suggested which describes a special mechanism for rotational deformation (plastic deformation accompanied by crystal lattice rotation) in nanocrystalline metals and ceramics. Within the model, the special rotational deformation occurs in a nanograin through formation of immobile disclinations whose strengths gradually increase during the formation process as a result of grain boundary sliding and diffusion. The conditions are calculated at which the special rotational deformation is energetically favorable in nanocrystalline Ni,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) and TiN-based ceramics.

© 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

**Keywords:** Rotational deformation; Plastic deformation; Nanocrystalline materials; Disclinations

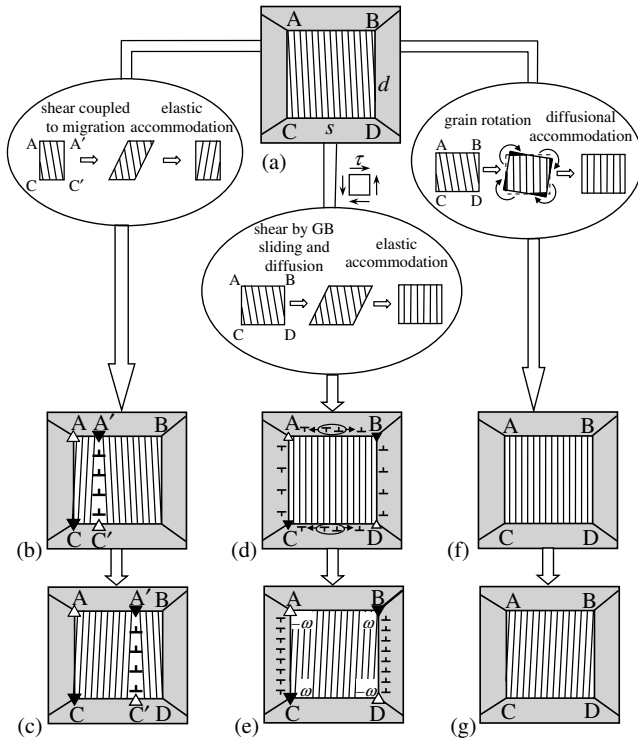
Plastic deformation mechanisms in nanocrystalline metals and ceramics showing outstanding mechanical properties are the subject of rapidly growing research efforts (e.g. [1–5]). It has been recognized that, in parallel with conventional lattice dislocation slip, alternative deformation mechanisms are capable of essentially or even crucially contributing to plastic flow of nanocrystalline materials (NCMs). These alternative mechanisms are grain boundary (GB) sliding, twin deformation, Coble creep and rotational deformation [1–5]. The latter mechanism represents plastic deformation accompanied by crystal lattice rotations. In particular, following experimental data [6–16], computer simulations [17–20] and theoretical models [21,22], stress-driven GB migration (carrying athermal grain growth) is treated as a rotational deformation mechanism effectively operating in NCMs. Furthermore, crystal lattice rotations in nanograins without GB migration were experimentally observed in NCMs during plastic deformation [1,23,24]. Elemental carriers of rotational deformation in NCMs are treated as interfacial wedge disclinations [7,21,25–27]. A wedge disclination represents a rotational line defect located at either a GB or a triple junction of GBs and characterized by a disclination strength, the rotational misfit (angle gap) [27–29]. For instance, a wedge disclination at a tilt GB is the line dividing GB

fragments with different tilt misorientation angles, whose difference is the disclination strength. A wedge disclination exists at a triple junction of tilt boundaries if the sum of tilt misorientation angles of these boundaries is non-zero [27–29]. The non-zero sum (angle gap) serves as the disclination strength.

Following the standard view on rotational deformation in conventional coarse-grained polycrystals [28] and NCMs [27], an elemental act of rotational deformation is the movement of a dipole of wedge disclinations characterized by constant strengths of opposite signs  $\pm\omega$  (Fig. 1a–c). Within this standard view, the movement of disclination dipoles in NCMs is associated with such structural transformations as GB migration [21] (Fig. 1a–c) or dislocation emission from GBs [27]. The main aim of this paper is to suggest and theoretically describe a special (new) rotational deformation mechanism that operates in NCMs without disclination dipole movement. The special mechanism represents rotational deformation occurring in a nanograin through the formation of immobile disclinations at nanograin boundary junctions (Fig. 1a, d, and e). The mechanism is specified by a gradual increase in the strengths of the immobile disclinations during their formation process due to GB sliding and diffusion (Fig. 1a, d, and e).

Let us consider the geometric features of the special rotational deformation in NCMs. For simplicity, we restrict our consideration to a two-dimensional grain structure (which serves as a good model for columnar nanoscale structures of films and a first-approximation

\* Corresponding author. Tel.: +7 812 321 4764; fax: +7 812 321 4771; e-mail: [ovidko@def.ipme.ru](mailto:ovidko@def.ipme.ru)



**Figure 1.** Geometry of crystal lattice rotations in nanocrystalline materials. (a) Initial state containing a rectangular grain ABDC. (b, c) Standard rotational deformation occurs through generation and movement of wedge disclinations (triangles). The moving wedge disclinations are located at the ends A' and C' of migrating grain boundary. (d, e) Special rotational deformation occurs in a nanograin through formation of immobile disclinations (triangles) whose strengths gradually increase during the formation process conducted by grain boundary dislocation slip and climb. (g, f) Diffusion-accommodated grain rotation that does not contribute to plastic flow. The elliptical insets at the arrows in (a), (b), (d) and (f) highlight the corresponding micromechanisms for crystal lattice rotations in nanograins.

model for bulk NCMs) containing a rectangular nanograin. Within our model, when a nanocrystalline specimen is mechanically loaded, the special rotational deformation in the nanograin ABDC occurs through the formation of immobile disclinations whose strengths gradually increase (Fig. 1a, d, and e). In doing so, the formation and evolution of the wedge disclinations at the edges of the rectangular nanograin ABDC is realized by means of both GB sliding along GBs AB and CD and parallel diffusion. More precisely, GB sliding is carried by GB dislocations that are nucleated at GBs AB and CD and slip under the action of the applied shear stress over these GBs (Fig. 1d). In parallel with GB sliding, diffusion occurs (which is driven by the stresses arising in the course of GB sliding) and provides GB dislocation climb over the vertical GBs AC and BD (Fig. 1d and e). As a result, two GB dislocation walls of opposite signs form at the vertical GBs AC and BD (Fig. 1d and e). The formation of these dislocation walls results in plastic deformation of the grain. In addition, the GB dislocation walls create stresses and produce extra tilt misorientation of the vertical GBs AC and BD (Fig. 1d and e), compared to the initial state (Fig. 1a). Following the theory of defects in solids [28], finite GB

dislocation walls, AC and BD, create elastic stresses effectively approximated as those created by a quadrupole of wedge disclinations located at the nanograin edges A, B, C and D (Fig. 1d and e). The strength magnitudes of these disclinations gradually increase with the increase in the density of GB dislocations at the vertical GBs AC and BD.

Note that all the disclinations carrying the special rotational deformation (Fig. 1d and e) are immobile, in contrast to the disclinations carrying GB migration (Fig. 1b and c). Also, the special rotational deformation (Fig. 1a, d, and e) driven by mechanical stresses is different from grain rotations (Fig. 1a, f, and g) [30–32] driven by a release of the GB energy (dependent on the boundary misorientation parameters). Following Refs. [30–32], such grain rotations are completely accommodated by diffusion (Fig. 1f and g), do not create elastic stresses and do not contribute to plastic flow, in contrast to the special rotational deformation (Fig. 1a, d, and e).

Thus, following our geometric analysis, the special rotational deformation effectively occurs through the formation of a quadrupole of immobile wedge disclinations whose strengths gradually increase (see Fig. 1a, d, and e). Let us examine the energy characteristics of this special rotational mechanism in a plastically deformed nanocrystalline solid. Let the solid contain a rectangular nanograin with the dimensions  $s$  and  $d$ , located as shown in Figure 1a. Suppose that rotational deformation occurs in the nanograin under the shear stress  $\tau$  or, in other words, the grain is plastically sheared (through GB sliding and diffusion) in the  $xy$ -plane by an angle  $\omega$  (Fig. 1a, d, and e). This rotational deformation leads to the formation of a quadrupole of wedge disclinations with the strengths  $\pm\omega$  (Fig. 1e). The energy  $\Delta W$  associated with the formation of the quadrupole (per unit disclination length) is the sum of the quadrupole self-energy and the energy of its interaction with the shear stress  $\tau$ . (In doing so, we neglect the resistance to GB dislocation slip contributing to the formation of the disclination quadrupole, because it is commonly low, at least, at high temperatures.) In the standard approximation that the nanocrystalline specimen is an elastically isotropic solid, with the approach [21], we find:

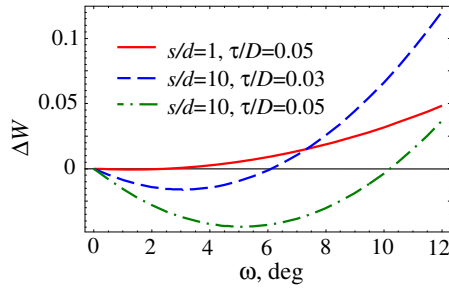
$$\Delta W = \frac{Dd^2}{2} \left\{ \omega^2 [(1+t^2) \ln(1+t^2) - t^2 \ln t^2] - \frac{2\omega\tau t}{D} \right\}, \quad (1)$$

where  $t = s/d$ ,  $D = G/[2\pi(1-\nu)]$ ,  $G$  is the shear modulus, and  $\nu$  is the Poisson's ratio.

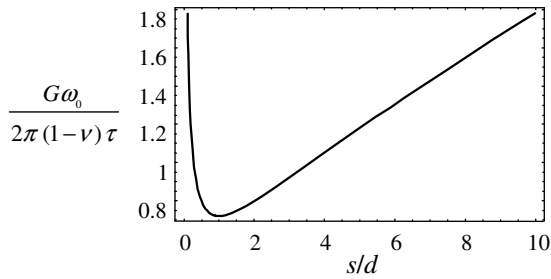
The dependences of  $\Delta W$  (in units of  $Dd^2/2$ ) on  $\omega$  are presented in Figure 2, for various values of the normalized stress  $\tau/D$  and grain aspect ratio  $s/d$ . Figure 2 shows that the energy  $\Delta W$  has a minimum at a certain (equilibrium) value  $\omega_0$  of the absolute disclination strength. The equilibrium disclination strength  $\omega_0$  is derived from the relation  $(\partial\Delta W/\partial\omega)|_{\omega=\omega_0} = 0$  as follows:

$$\omega_0 = \frac{\tau t}{D[(1+t^2) \ln(1+t^2) - t^2 \ln t^2]}. \quad (2)$$

The dependence of the parameter  $G\omega_0/[2\pi(1-\nu)\tau]$  on the grain aspect ratio  $s/d$  is shown in Figure 3. From Figure 3 it follows that the equilibrium disclination



**Figure 2.** Dependence of the energy change  $\Delta W$  associated with the formation of a disclination quadrupole (in units of  $Dd^2/2$ ) on the disclination strength  $\omega$ .



**Figure 3.** Dependence of the parameter  $G\omega_0/[2\pi(1-\nu)\tau]$  (characterizing the equilibrium disclination strength  $\omega_0$ ) on the grain aspect ratio  $s/d$ .

strength  $\omega_0$  is lowest for a equilateral grain (with  $s = d$ ) and increases with the increase in the ratio of the larger grain dimension to the smaller one. For the case of a grain in nanocrystalline Ni, we have [33]:  $G = 73$  GPa and  $\nu = 0.34$ . Then, for the typical flow stress  $\tau = 0.5$  GPa, from formula (2) one obtains:  $\omega_0 \approx 0.02 \approx 1.2^\circ$  for  $s/d = 1$ , and  $\omega_0 \approx 0.05 \approx 2.9^\circ$  for  $s/d = 10$  or  $1/10$ . For the case of nanocrystalline  $\alpha\text{-Al}_2\text{O}_3$  (corundum) with  $G = 169$  GPa and  $\nu = 0.23$  [34] and  $\tau = 1$  GPa, we obtain:  $\omega_0 \approx 1.2^\circ$  for  $s/d = 1$ , and  $\omega_0 \approx 2.9^\circ$  for  $s/d = 10$  or  $1/10$ . For the case of a grain in nanocrystalline TiN-based coatings [35] (whose elastic moduli are approximated by the elastic constants,  $G = 240$  GPa and  $\nu = 0.25$ , of TiN) and  $\tau = 3$  GPa, we have:  $\omega_0 \approx 2.5^\circ$  and  $6^\circ$  for  $s/d = 1$  and  $10$ , respectively.

Let us roughly estimate the plastic strain associated with the special rotational deformation in NCMs. Let rotational deformation in a grain be associated with the formation of  $n$  GB dislocation dipoles with a Burgers vector magnitude  $b$  at the vertical GBs AC and BD (Fig. 1e). According to the Orowan formula [36], these dislocation dipoles create the plastic shear strain  $\gamma_g = nb/d$  inside the grain. At the same time, the formation of  $n$  GB dislocation dipoles is equivalent to the formation of a quadrupole of wedge disclinations with strengths  $\pm\omega$  (Fig. 1e). Hence,  $nb/d$  has the following relation to the disclination strength  $\omega$ :  $nb/d = 2\tan(\omega/2)$  or, in the typical situation where  $\omega$  is low,  $nb/d \approx \omega$  [28]. As a corollary, in the case we are considering here (Fig. 1e), the plastic strain in the plastically deformed grain is  $\gamma_g \approx \omega$ . With this approximate relation and the above estimates of  $\omega$  in nanocrystalline Ni,  $\alpha\text{-Al}_2\text{O}_3$  and TiN-based ceramics, one finds that  $\gamma_g$  ranges from

0.02 to 0.1. These values of the plastic strain inside grains deformed by the special rotational mechanism are close to the total macroscopic strain  $\varepsilon$  ( $\varepsilon \approx 0.02\text{--}0.05$ ; see Refs. [1–5]) at which most NCMs are fractured. Thus, the special rotational mechanism is capable of significantly contributing to the plastic strain of real NCMs, if the fraction  $F$  of grains deformed by this mechanism is large enough.

Let us derive the stress–strain relationship for NCMs deformed solely by the special rotational mechanism. For simplicity, assume that all the grains represent identical squares with sides of length  $d$  and deform independently of each other. In general, the average strain created by the plastically deformed grains depends on the kind of loading and orientations of grain facets with respect to the loading direction(s). However, as a first approximation, we can put  $\varepsilon \approx F\gamma_g$ , where  $\varepsilon$  is the mean macroscopic strain created by the rotational deformation. In this case, with formula (2) (taken for  $\nu = 0.3$  and  $t = 1$ ) and the relation  $\omega_0 \approx \gamma_g$ , one finds:

$$\frac{\tau}{G} \approx \frac{0.3\varepsilon}{F}. \quad (3)$$

For example, formula (3) gives:  $\tau/G \approx (3/2)\varepsilon$ , for  $F = 0.2$ , and  $\tau/G \approx 0.6\varepsilon$ , for  $F = 0.5$ .

The strain hardening described by formula (3) is attributed to the storage of GB dislocations at GBs (e.g. vertical GBs AB and CD shown in Fig. 1d and e) during special rotational deformation. The GB dislocations form finite walls (Fig. 1d and e) creating stress fields that hamper further dislocation nucleation and movement in both the interior regions of nearest nanograins and their GBs. This hampering effect increases when the density of GB dislocations in the walls (or, in other words, the absolute value  $\omega$  of the strengths of the corresponding disclinations) grows. The hampering effect is specified by the length scale equal to the screening length for the stress fields of disclinations forming a quadrupole. The screening length is around the interspacing between the nearest disclinations [27,28]. The latter is around the grain size (Fig. 1d and e), in which case the hampering effect contributes to strain hardening on the grain size level in NCMs. At the same time, the special rotational deformation is carried by GB sliding and diffusion, which are thermally activated and can therefore be considered as rate-limiting processes (Fig. 1a, d, and e). Thus, the special rotational deformation represents a rate-limiting deformation mechanism which produces strain hardening on the grain size level in NCMs.

Note that the strain hardening attributed to the storage of GB dislocations at GBs is inherent to NCMs. As with the special rotational deformation, other deformation mechanisms (say, emission of lattice dislocations from GBs, their transfer across grain interiors and absorption at opposite GBs [3–5,20]) create excess GB dislocations at GBs in NCMs. The strain hardening attributed to the storage of GB dislocations in NCMs is different from the strain hardening attributed to the storage of lattice dislocations in grain interiors in coarse-grained polycrystals. Furthermore, note that the special rotational deformation is carried by both GB sliding and diffusion, which are intensive in NCMs in

certain situations. In particular, GB sliding and associated diffusion processes play a dominant role in superplastic deformation of ultrafine-grained solids and NCMs [1,5,37–39]. In addition, GB diffusional creep (Coble creep) and GB sliding serve as rate-limiting deformation mechanisms that effectively operate at low stresses and strain rates [4,40]. GB sliding is also intensive at very high stresses and strain rates (see Ref. [3] and references therein). In this context, one expects the special rotational deformation to be capable of making a crucial contribution to plastic flow of NCMs in the situations discussed.

To summarize, we have suggested a theoretical model describing a special mechanism for rotational deformation in nanocrystalline metals and ceramics. The special rotational deformation occurs in a nanograin through the formation of immobile disclinations whose strengths gradually increase during the formation process as a result of both grain boundary sliding and diffusion. This mechanism is different from both standard rotational deformation, which occurs through the movement of wedge disclinations, and diffusion-accommodated grain rotations, which do not contribute to plastic flow. It is theoretically shown that the special rotational deformation is energetically favorable in nanocrystalline Ni,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiN-based ceramics over wide ranges of structural parameters and mechanical loads.

The work was supported, in part, by the Russian Federal Agency of Science and Innovations (Contract 02.513.11.3190), the National Science Foundation (grant CMMI # 0700272), Russian Academy of Sciences Program “Structural Mechanics of Materials and Construction Elements”, and the Russian Foundation of Basic Research (grant 08-01-00225-a).

- [1] A.K. Mukherjee, Mater. Sci. Eng. A 322 (2002) 1.
- [2] K.S. Kumar, S. Suresh, H. Swygenhoven, Acta Mater. 51 (2003) 5743.
- [3] D. Wolf, V. Yamakov, S.R. Phillpot, A.K. Mukherjee, H. Gleiter, Acta Mater. 53 (2005) 1.
- [4] M. Dao, L. Lu, R.J. Asaro, J.Th.M. De Hosson, E. Ma, Acta Mater. 55 (2007) 4041.
- [5] C.C. Koch, I.A. Ovid'ko, S. Seal, S. Veprek, Structural Nanocrystalline Materials: Fundamentals and Applications, Cambridge University Press, Cambridge, 2007.
- [6] M. Jin, A.M. Minor, E.A. Stach, J.W. Morris Jr., Acta Mater. 52 (2004) 5381.
- [7] W.A. Soer, J.Th.M. De Hosson, A.M. Minor, J.W. Morris Jr., E.A. Stach, Acta Mater. 52 (2004) 5783.
- [8] J.T.M. De Hosson, W.A. Soer, A.M. Minor, Z. Shan, E.A. Stach, S.A. Syed Asif, O.L. Warren, J. Mater. Sci. 41 (2006) 7704.
- [9] K. Zhang, J.R. Weertman, J.A. Eastman, Appl. Phys. Lett. 85 (2004) 5197;
- [10] P.L. Gai, K. Zhang, J. Weertman, Scripta Mater. 56 (2007) 25.
- [11] X.Z. Liao, A.R. Kilmametov, R.Z. Valiev, H. Gao, X. Li, A.K. Mukherjee, J.F. Bingert, Y.T. Zhu, Appl. Phys. Lett. 88 (2006) 021909.
- [12] D. Pan, T.G. Nieh, M.W. Chen, Appl. Phys. Lett. 88 (2006) 161922.
- [13] D. Pan, S. Kuwano, T. Fujita, M.W. Chen, Nano Lett. 7 (2007) 2108.
- [14] D.S. Gianola, S. Van Petegem, M. Legros, S. Brandstetter, H. Van Swygenhoven, K.J. Hemker, Acta Mater. 54 (2006) 2253.
- [15] D.S. Gianola, D.H. Warner, J.F. Molinari, K.J. Hemker, Scripta Mater. 55 (2006) 649.
- [16] G.J. Fan, L.F. Fu, H. Choo, P.K. Liaw, N.D. Browning, Acta Mater. 54 (2006) 4781.
- [17] D. Farkas, A. Froseth, H. Van Swygenhoven, Scripta Mater. 55 (2006) 695.
- [18] J. Monk, D. Farkas, Phys. Rev. B 75 (2007) 045414.
- [19] F. Sansoz, V. Dupont, Appl. Phys. Lett. 89 (2006) 111901.
- [20] T. Shimokawa, A. Nakatani, H. Kitagawa, Phys. Rev. B 71 (2005) 224110.
- [21] M.Yu. Gutkin, I.A. Ovid'ko, Appl. Phys. Lett. 87 (2005) 251916.
- [22] J.C.M. Li, Phys. Rev. Lett. 96 (2006) 215506.
- [23] M. Ke, W.W. Milligan, S.A. Hackney, J.E. Carsley, E.C. Aifantis, Nanostruct. Mater. 5 (1995) 689.
- [24] Zh. Shan, E.A. Stach, J.M.K. Wiezorek, J.A. Knapp, D.M. Follstaedt, S.X. Mao, Science 305 (2004) 654.
- [25] M. Murayama, J.M. Howe, H. Hidaka, S. Takaki, Science 295 (2002) 2433.
- [26] I.A. Ovid'ko, Science 295 (2002) 2386.
- [27] M.Yu. Gutkin, I.A. Ovid'ko, Plastic Deformation in Nanocrystalline Materials, Springer Verlag, Berlin, 2004.
- [28] A.E. Romanov, V.I. Vladimirov, in: F.R.N. Nabarro (Ed.), Dislocations in Solids, vol. 9, Amsterdam, North Holland, 1992, pp. 191–402.
- [29] G. Dimitrakopoulos, Ph. Komminou, Th. Karakostas, R.C. Pond, Interface Sci. 7 (1999) 217.
- [30] J.C.M. Li, J. Appl. Phys. 33 (1962) 2958.
- [31] K.E. Harris, V.V. Singh, A.H. King, Acta Mater. 46 (1998) 2623.
- [32] D. Moldovan, D. Wolf, S.R. Phillpot, Acta Mater. 49 (2001) 3521.
- [33] C.J. Smithells, E.A. Brads, Metals Reference Book, Butterworth, London, 1976.
- [34] R.G. Munro, J. Am. Ceram. Soc. 80 (1997) 1919.
- [35] S. Veprek, Rev. Adv. Mater. Sci. 5 (2003) 6.
- [36] E. Orowan, Proc. Phys. Soc. 52 (1940) 8.
- [37] K.A. Padmanabhan, H. Gleiter, Mater. Sci. Eng. A 381 (2004) 28.
- [38] R.Z. Valiev, Nature Mater. 3 (2004) 511.
- [39] X. Xu, T. Nishimura, N. Hirotsaki, R.J. Xie, Y. Yamamoto, H. Tanaka, Acta Mater. 54 (2006) 255.
- [40] J. Weissmüller, J. Markmann, Adv. Eng. Mater. 7 (2005) 202.