

# Nucleation of nanograins near cracks in nanocrystalline materials

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Nucleation of nanograins near crack tips and its role as a special (new) toughening mechanism in deformed nanocrystalline materials are theoretically described. Within our description, stress-driven splitting and migration of grain boundaries occur near crack tips. These stress-driven processes result in nucleation of nanograins and cause a partial stress relaxation near cracks. It is shown that the nucleation of nanograins near crack tips is energetically favorable and effective in enhancing toughness in nanocrystalline ceramic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

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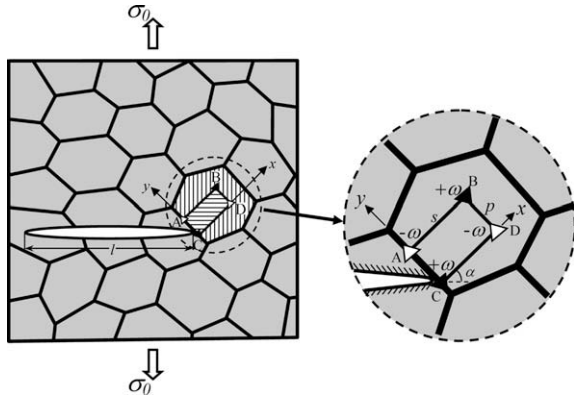
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Nanocrystalline materials (NCMs) exhibit super-strength and superhardness, but, in most cases, at the expense of low ductility and low fracture toughness [1–7]. The mechanical properties of NCMs are dictated by their specific structural features such as nanoscale grain sizes and large numbers of interfaces. In particular, due to the specific structural features, the conventional lattice slip (which dominates in coarse-grained polycrystalline metals showing good ductility) is suppressed, and alternative deformation mechanisms effectively operate in NCMs [1–7]. The alternative deformation mechanisms in NCMs are considered to be intergrain sliding, twin deformation, grain boundary (GB) diffusional creep and rotational deformation [1–7]. Recently, a new deformation mechanism, the namely stress-driven GB migration leading to grain growth, has been experimentally revealed in NCMs [8–13]; see also theoretical models [14–16] and computer simulations [17,18]. In theoretical papers [14–16], the stress-driven GB migration was described as a deformation mechanism associated with formation and evolution of wedge disclinations, rotational defects at GBs. The experiments [8–13], theoretical models [14–16] and computer simulations [17,18] were focused

on stress-driven migration of pre-existing GBs that results in grain growth in deformed NCMs. At the same time, the stress-driven migration of GBs can also cause nucleation of new nanoscale grains and thereby grain refinement—a phenomenon opposite to grain growth—in deformed coarse-grained polycrystals [19] and NCMs [20]. In the latter case, following theoretical analysis [20], the migration should be preceded by splitting of pre-existent GBs, and the nanograin nucleation serves as a special deformation mechanism in NCMs. In the context discussed, since the stress-driven GB migration leading to grain growth was theoretically recognized as that capable of enhancing the fracture toughness of NCMs [16], of great interest are the effects of the stress-driven nanograin nucleation on fracture toughness in NCMs. The main aim of this paper is to theoretically describe nanograin nucleation near crack tips as a special (new) toughening mechanism in NCMs.

Let us consider a nanocrystalline solid which has the mean grain size  $d$ , contains a mode I crack and is subjected to one-axis tensile load  $\sigma_0$ . A two-dimensional section of the solid with a flat crack of length  $l$  is schematically shown in Figure 1. For simplicity, we assume that the defect structure of the solid is the same along the coordinate axis  $z$  perpendicular to the  $xy$  plane shown in Figure 1. This assumption will allow us to simplify the mathematical analysis of the problem in our study (theoretical

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**Figure 1.** Formation of new nanoscale grain and associated disclination quadrupole near crack tip in deformed nanocrystalline solid.

description of the nanograin nucleation and its effects on crack growth in NCMs), reducing it to the consideration of a two-dimensional structure. At the same time, the two-dimensional description definitely reflects the key aspects of the problem. In the two-dimensional picture (Fig. 1), the crack grows along the axis  $x$  and is located in the region  $0 < x < l$ . In addition, the specimen is assumed to be an elastically isotropic solid, having shear modulus  $G$  and Poisson ratio  $\nu$ .

Let  $\sigma_{ij}^c$  be the stress field created by the external load  $\sigma_0$  in the solid with the crack. We think that the shear stress component  $\sigma_{xy}^c$  can cause nucleation of a new nanoscale grain near the crack tip (Fig. 1). Following this approach [20], the nanograin nucleation can serve as a special deformation mechanism occurring through three processes (i) splitting of a pre-existing GB fragment  $A'C'$  (not shown in Fig. 1) into immobile boundary  $AC$  (located on the same place as the pre-existent GB  $A'C'$ ) and mobile boundary  $BD$ ; (ii) migration of GB  $BD$ ; (iii) formation of two new grain boundaries  $AB$  and  $CD$  (Fig. 1). As with grain growth occurring through GB migration coupled to shear in NCMs [16,20], migration of GB  $BD$  is coupled to shear hampered by the surrounding material, and the hampered shear results in formation of a quadrupole  $ABCD$  of wedge disclinations with strengths  $\pm\omega$  (Fig. 1). The newly formed grain  $ABCD$  can be shaped as either a rectangle or a lozenge, depending on the shape of the area swept by the migrating boundary  $BD$ . We consider a rectangular grain  $ABCD$  with sizes  $s$  and  $p$  serving also as distances between the disclinations (Fig. 1). Its orientation relative to the crack plane is specified by angle  $\alpha$  (Fig. 1).

The nanograin nucleation (Fig. 1) is characterized by the energy difference  $\Delta W = W_2 - W_1$ , where  $W_1$  is the energy of the solid in its initial state containing the crack, and  $W_2$  is the energy of the solid in its final state containing both the crack and new nanograin. The nanograin nucleation is energetically favorable, if  $\Delta W < 0$ . The energy difference  $\Delta W$  (per unit length along the axis  $z$ ) can be represented as the sum of the three terms:

$$\Delta W = E^q + E^{q-\sigma} + \Delta E_{gb}, \quad (1)$$

where  $E^q$  is the proper energy of the disclination quadrupole,  $E^{q-\sigma}$  is the energy that characterizes the interaction

between the disclination quadrupole and the shear stress field  $\sigma_{ij}^c$  created by the external tensile load  $\sigma_0$  in the solid containing the crack, and  $\Delta E_{gb}$  is the difference in the energy of GBs between the final and initial states.

In a first approximation (neglecting the effects of the crack on the disclination quadrupole stresses), the proper energy  $E^q$  of the disclination quadrupole is given by the following standard expression [21] for the disclination quadrupole energy in an infinite, elastically isotropic solid:

$$E^q = \frac{D\omega^2 p^2}{2} ((1+t^2) \ln[1+t^2] - t^2 \ln t^2), \quad (2)$$

where  $t = s/p$ . The energy  $E^{q-\sigma}$  figuring in formula (2) is written as follows [22]:

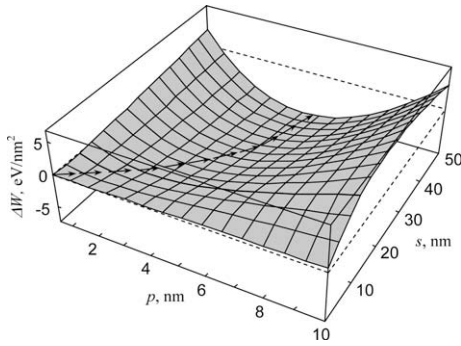
$$E^{q-\sigma} = -\omega \int_S \sigma_{xy}^c dS', \quad (3)$$

where  $S$  is the area bounded by the disclination quadrupole,  $S'$  is the integration parameter, and  $\sigma_{xy}^c$  is a component of the stress field  $\sigma_{ij}^c$  (in the coordinate system  $(x, y)$ ; see Fig. 1) created by the external tensile load  $\sigma_0$  in the solid containing the crack. The expression for  $\sigma_{xy}^c$  can be found in Ref. [23].

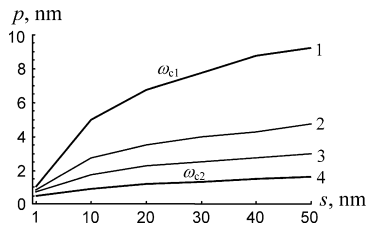
The GB energy difference  $\Delta E_{gb}$  is given by formula:  $\Delta E_{gb} = s\gamma_{AB} + p\gamma_{AC} + s\gamma_{CD} + p\gamma_{BD} - p\gamma_{A'C'}$ , where  $\gamma_{AB}$ ,  $\gamma_{CD}$ ,  $\gamma_{BD}$  and  $\gamma_{AC}$  are the specific energies (per unit area of GB plane) of new boundaries  $AB$ ,  $CD$ ,  $BD$  and  $AC$ , while  $\gamma_{A'C'}$  denotes the specific energy of the pre-existing boundary  $A'C'$ . In general, the specific energies are sensitive to GB misorientation parameters. Because of space limitations, we focus our examination on a partial situation where all the GBs under consideration are high-angle general symmetric tilt boundaries. For such (widespread) GBs in many materials, the energy  $\gamma$  vs. tilt misorientation  $\theta$  is a slowly increasing or approximately constant function of  $\theta$  [24]. In this context, for simplicity, we assume that all the GB energies are the same:  $\gamma_{AB} = \gamma_{AC} = \gamma_{CD} = \gamma_{BD} = \gamma_{A'C'} = \gamma_b$ . With this assumption, we have

$$\Delta E_{gb} = \gamma_b(2s + p) \quad (4)$$

Eqs. (1)–(4) allow the energy difference  $\Delta W$  to be found. Let us use these formulas in order to calculate the dependence of the energy difference  $\Delta W$  on the sizes  $s$  and  $p$  of the new nanograin in the example case of nanocrystalline ceramic  $\alpha$ - $\text{Al}_2\text{O}_3$ . In our calculations, we use the following typical values of parameters of  $\alpha$ - $\text{Al}_2\text{O}_3$  [25]:  $G = 169$  GPa,  $\nu = 0.23$ ,  $\gamma = 1.5$  J m $^{-2}$  [13],  $\gamma_b = 0.5$  J m $^{-2}$  [26]. The external stress  $\sigma_0$  is supposed to be equal to 1 GPa; this value is typical for mechanical tests of nanocrystalline ceramics. The crack length  $L$  is chosen as  $L = 800$  nm. This value is close to (but slightly lower than) the Griffith crack length in  $\alpha$ - $\text{Al}_2\text{O}_3$  at the considered stress level. The characteristic angle is chosen as  $\alpha = 70^\circ$ , because the shear stress concentrated near a crack tip in a solid under tensile load is maximum [27] (and thereby the formation of the new nanograin is most energetically favorable) at this value of  $\alpha$ . Figure 2 presents the dependences  $\Delta W(s, p)$ , calculated by Eqs. (1)–(4) for above specified parameters of nanocrystalline



**Figure 2.** Dependence of the energy difference  $\Delta W$  on the nanograin sizes  $s$  and  $p$ .



**Figure 3.** Dependence of the equilibrium size  $p_{eq}$  on the size  $s$  and  $p$ , for various values of the disclination strength  $\omega = 3^\circ, 5^\circ, 7^\circ$  and  $11^\circ$  (curves 1, 2, 3 and 4, respectively).

$\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Arrows in Figure 2 show evolution in the space  $(s, p)$ , corresponding to the most energetically favorable formation/growth of the new nanograin.

It follows from Figure 2 that the most energetically favorable growth of the new nanograin is specified by a simultaneous increase in the nanograin sizes  $s$  and  $p$ . That is, for any value of the size  $s$ , the equilibrium rectangular shape (corresponding to the minimum energy difference  $\Delta W(s, p)$  of the new nanograin) is specified by the equilibrium size  $p_{eq}$ . We calculated the dependence  $p_{eq}(s)$  of the equilibrium size  $p_{eq}$  on the size  $s$ , for various values of the disclination strength  $\omega$  (Fig. 3). From Figure 3, it follows that the equilibrium shape of the new nanograin tends to be a highly elongated rectangle with the ratio  $s/p_{eq} \gg 1$ . Note that the formation of the new nanograin and associated disclination quadrupole is energetically favorable if the disclination strength  $\omega$  is within the interval  $\omega_{c1} \leq \omega \leq \omega_{c2}$ . Curves 1 and 4 in Figure 3 correspond to the lowest and highest levels of the critical disclination strength,  $\omega_{c1} = 3^\circ$  and  $\omega_{c2} = 11^\circ$ , respectively.

Now let us turn to consideration of the nanograin nucleation effects on crack growth. Any crack in a solid is characterized by its critical (Griffith) length defined as the minimum length at which catastrophic growth of the crack occurs at given stress level [27]. When the critical length of a crack increases, so does stability of the crack relative to its catastrophic growth. Let us calculate the critical length  $l_c$  of an intragranular mode I crack that grows under superposition of the external load stress  $\sigma_0$  and the stress field of the disclination quadrupole, as is shown in Figure 1. For our calculations, we will use the force criterion (e.g. [27]):

$$K_I(l = l_c) = K_{IC}, \quad (5)$$

where  $K_I$  is the stress intensity factor given by the formula [14]:

$$K_I(l) = \sqrt{\frac{2}{\pi l}} \int_0^l \sigma_{yy}(x, y = 0) \sqrt{\frac{x}{l-x}} dx, \quad (6)$$

where  $\sigma_{yy}$  is the stress tensor component created by the external load and the disclination quadrupole in the solid in the absence of crack, and  $K_{IC}$  is the critical value of the stress intensity factor. In the situation with a mode I crack in an isotropic solid, one has:

$$K_{IC} = \sqrt{\frac{4\gamma G}{1-\nu}}, \quad (7)$$

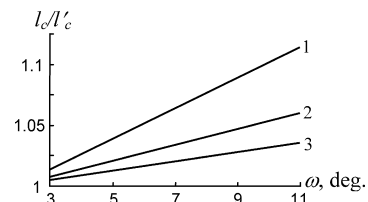
where  $\gamma$  is the specific energy (per unit area) of the crack free surface. The stress  $\sigma_{yy}$  in Eq. (2) can be represented as the sum  $\sigma_{yy} = \sigma_{yy}^d + \sigma_0$ , where  $\sigma_{yy}^d$  is the stress tensor component created by the disclination quadrupole. This component can be easily calculated using formulas [22].

Eqs. (5)–(7) allow one to numerically calculate the critical crack length  $l_c$  of a crack growing in the superposition of both the external tensile stress  $\sigma_0$  and the stress field created by the disclination quadrupole. In a partial case of  $\omega = 0$  (when the disclination quadrupole is absent, and  $\sigma_{yy}(x, y) = \sigma_0$ ), Eqs. (5)–(7) give the following well-known expression for the critical length  $l'_c = l_c(\omega = 0)$  of a mode I crack growing under the action of the external tensile load only:

$$l'_c = \frac{8G\gamma}{\pi(1-\nu)\sigma_0^2}. \quad (8)$$

The ratio  $l_c/l'_c$  quantitatively characterizes the effect of the nanograin nucleation (Fig. 1) on crack growth. (Fracture toughness due to the nanograin formation increases if the ratio  $l_c/l'_c > 1$ ; and decreases if  $l_c/l'_c < 1$ .) In the case of nanocrystalline ceramic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with the previously specified parameters, we calculated the dependence of the characteristic ratio  $l_c/l'_c$  on the disclination strength  $\omega$  from the range  $\omega_{c1} \leq \omega \leq \omega_{c2}$  (specifying the energetically favorable formation of nanograins), for various values of the nanograin size  $s$  (Fig. 4). As it follows from the dependences  $l_c/l'_c(\omega)$  in Figure 4, the critical length of a crack grows or, in other words, the fracture toughness of nanocrystalline ceramic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is enhanced, when the disclination strength  $\omega$  increases and/or the nanograin size  $s$  decreases.

Thus, formation of new nanoscale grains and associated disclination quadrupoles near crack tips in NCMs (Fig. 1) relieves, in part, stresses concentrated near these tips. This process leads to moderate enhancement of fracture toughness. The process involves splitting of



**Figure 4.** Dependences of the ratio  $l_c/l'_c$  of critical crack lengths on the disclination strength  $\omega$ , for various values of the nanograin size  $s = 10, 20$  and  $30$  nm (curves 1, 2 and 3, respectively).

GBs (Fig. 1) and thereby is enhanced in NCMs in which the volume fractions occupied by GBs are very large. Furthermore, the stress-driven nanograin nucleation in nanocrystalline ceramics is expected to be more effective as a deformation and toughening mechanism, compared to the stress-driven grain growth, because migration of pre-existing GBs in nanoceramics is often suppressed by the difference in the chemical composition between the grain interiors and GBs [28].

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