

# EFFECTS OF TRANSFORMATIONS OF GRAIN BOUNDARY DEFECTS ON DIFFUSION IN NANOCRYSTALLINE MATERIALS

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**Abstract.** The specific features of diffusion processes in nanocrystalline materials are discussed. Theoretical models are suggested that describe the effects of transformations (climbing, splitting) of grain boundary dislocations and disclinations on self-diffusion in nanocrystalline materials. It is shown that climbing of grain boundary dislocations strongly enhances diffusion processes in nanocrystalline materials, causing the self diffusion coefficient to be increased by several orders.

## 1. INTRODUCTION

Nanocrystalline materials are the subject of intensive theoretical and experimental studies motivated by extremely high importance of their applications; see, e.g. [1-5]. Nanocrystalline materials synthesized at highly non-equilibrium conditions exhibit the anomalously enhanced diffusional properties [2, 6-10]. For instance, the self diffusion coefficients in nanocrystalline fcc materials are about 2 to 4 orders of magnitude larger than the grain boundary self diffusion coefficients in conventional polycrystalline fcc materials with the same chemical composition [2, 6-10]. As noted by Gleiter [2], anomalously fast diffusion in nanocrystalline materials is related to the three following factors: (i) Rigid body relaxation of grain boundaries that occurs via relative translational displacements of their adjacent crystallites and reduces the boundary free volume is hampered in nanocrystalline materials. (This is related to the fact that rigid body relaxations of the various boundaries surrounding every nanocrystallite require its different displacements due to their different atomic structure.) (ii) The self diffusion in nanocrystalline materials is essentially enhanced due to the existence of high-density network of grain boundary junction tubes which commonly are characterized by more increased diffusion rate than grain boundaries themselves. (iii) In grain boundaries of nanocrystalline materials the concentration of impurities that often reduce boundary

diffusivity is lower than that in grain boundaries in conventional polycrystals.

However, together with factors (i)-(iii), the existence and transformations of ensembles of grain boundary dislocations and disclinations are capable of strongly enhancing the diffusion processes in nanocrystalline materials. The main aim of this paper is to elaborate theoretical models that describe the role of transformations of grain boundary defects in anomalously fast diffusion in nanocrystalline materials.

## 2. ROLE OF GRAIN BOUNDARY DEFECTS IN ENHANCED DIFFUSION PROCESSES IN NANOCRYSTALLINE MATERIALS. GENERAL ASPECTS

Let us discuss the specific features of diffusion in nanocrystalline materials in more details. The coefficient of self diffusion occurring via transfer of vacancies<sup>1</sup> is given as (e.g., [11]):

$$D = D_0 \exp \left[ \frac{(\epsilon_f + \epsilon_m)}{kT} \right], \quad (1)$$

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<sup>1</sup> In general, diffusion processes in crystals occur via transfer of point defects of different types. However, self diffusion occurring via transfer of vacancies is most effective; it is characterized by the largest coefficient of diffusion, e.g., [11].

where  $D_0$  denotes the constant dependent on parameters of the ideal crystalline lattice,  $k$  the Boltzmann's constant,  $T$  the absolute temperature,  $\epsilon_f$  and  $\epsilon_m$  the energies of respectively formation and migration of vacancies. In nanocrystalline materials (characterized by extremely high volume fraction of the grain boundary phase) self-diffusion processes occur mostly via transfer of grain boundary vacancies. In these circumstances, all the factors (i)-(iii) discussed in introductory section induce the characteristic boundary free volume to be increased and, as a corollary, both formation and migration of boundary vacancies to be facilitated ( $\epsilon_f$  and  $\epsilon_m$  to be decreased) in nanocrystalline materials as compared to those in conventional polycrystals. In terms of formula (1), the self diffusion coefficient  $D$  is increased in nanocrystalline materials, because their characteristic energies,  $\epsilon_f$  and  $\epsilon_m$ , are decreased due to factors (i)-(iii) discussed in paper [2].

We think that, together with factors (i)-(iii), the existence and transformations of ensembles of grain boundary dislocations and disclinations strongly enhance diffusion processes in nanocrystalline materials. The effects of such defects on diffusion are briefly as follows:

- (a) Cores of grain boundary dislocations and disclinations are characterized by excess free volume, in which case their presence in grain boundaries increases the total free volume that characterizes the grain boundary phase in nanocrystalline materials. This decreases values of  $\epsilon_f$  and  $\epsilon_m$  and, therefore, enhances diffusion processes occurring by vacancy mechanism.
- (b) Disorderedly distributed grain boundary dislocations and disclinations are formed in nanocrystalline materials synthesized at highly non-equilibrium conditions. Such dislocations and disclinations rearrange to annihilate or to form more ordered, low-energy configurations, in which case they move to new positions. Climbing of (grain boundary) dislocations is accompanied by generation of new point defects [11] - vacancies and interstitial atoms - serving as new carriers of diffusion. In this situation, generation of new vacancies occurs under the action of the driving force related to a release of the elastic energy of "non-equilibrium" grain boundary dislocations and disclinations during their transformations. The action of the driving force in question facilitates diffusion processes in nanocrystalline materials. The effect discussed is quantitatively described by formula (1) with the sum  $\epsilon_f + \epsilon_m$  being replaced by  $\epsilon_f - W + \epsilon_m$  where  $W (>0)$  is the energy release due to climbing of a grain boundary dislocation, per one vacancy emitted by the dislocation.
- (c) Dilatation stress fields of grain boundary dislocations and disclinations influence migration of va-

cancies. More precisely, the elastic interaction between vacancies and grain boundary dislocations and disclinations is characterized by the energy [12]:

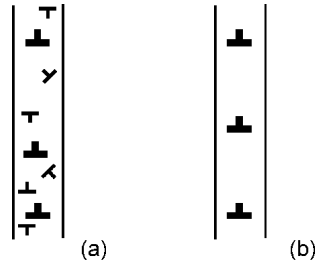
$$\epsilon_{int} = \frac{-\sigma_{ii} \Delta V}{3}, \quad (2)$$

where  $\sigma_{ii}$  denotes the sum of dilatation components (say, components  $\sigma_{xx}$ ,  $\sigma_{yy}$  and  $\sigma_{zz}$  written in  $(x, y, z)$  - coordinates) of stress fields created by grain boundary defects, and  $\Delta V$  the excess free volume associated with a vacancy. To minimize  $\epsilon_{int}$ , vacancies migrate to regions where compressive stresses exist. This vacancy migration contributes to enhanced diffusion in nanocrystalline materials. The effect discussed is quantitatively described by formula (1) with the sum  $\epsilon_f + \epsilon_m$  being replaced by the sum  $\epsilon_f + \epsilon_m + \epsilon_{int}$ .

In next section we will examine the effects of grain boundary defect transformations on diffusion in nanocrystalline materials in several characteristic cases. These transformations are climbing of grain boundary dislocations composing dipole configurations (section 3), splitting of grain boundary disclinations (section 4) and the splitting of grain boundary dislocations, which is associated with the formation of amorphous intergranular layers in nanocrystalline materials (section 5).

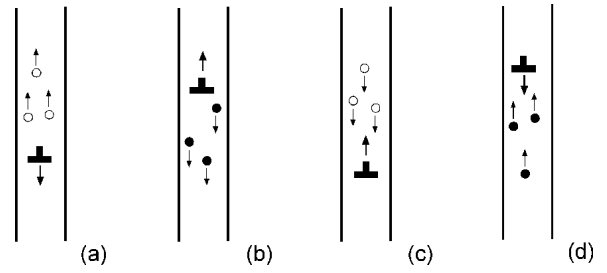
### 3. CLIMBING OF GRAIN BOUNDARY DISLOCATIONS AND DIFFUSION IN NANOCRYSTALLINE MATERIALS

Nanocrystalline materials are often synthesized at highly non-equilibrium conditions (see, e.g., [1-5]), in which case "non-equilibrium" defect structures are formed at grain boundaries. In particular, grain boundaries in such materials contain not only geometrically necessary dislocations (that is, grain boundary dislocations associated with the mean boundary misorientation; see, e.g., [13, 14]), but also the so called "excess" grain boundary dislocations (that provide local deviations of the boundary misorientation from its mean value and commonly are chaotically distributed along a grain boundary) (Fig. 1a). In addition, owing to highly non-equilibrium conditions of synthesis, the geometrically necessary dislocations, generally speaking, are disorderedly displaced relative to their "equilibrium" positions (Fig. 1a). During some relaxation period after synthesis of a nanocrystalline sample, transformations of the ensemble of grain boundary dislocations occur leading to a release of its elastic energy. In doing so, the "excess" dislocations with opposite Burgers vectors move (climb and glide) to each other and annihilate, and the geometrically necessary dislocations move (climb plus glide) to their equilibrium positions (Fig. 1b).



**Fig. 1.** Dislocation ensembles at (a) non-equilibrium and (b) equilibrium high-angle grain boundaries.

The climbing of grain boundary dislocations during the relaxation period is accompanied by both emission and absorption of point defects: vacancies and interstitial atoms (Fig. 2). In these circumstances, emission of vacancies (“take-off” of vacancies from dislocation cores and their consequent displacement into the surrounding grain boundary phase; see Fig. 2a) is more intensive than that of interstitial atoms (Fig. 2b), because vacancies are essentially more mobile compared to interstitial atoms [11]. Also, it should be noted that absorption of vacancies, which accompanies the climbing of grain boundary dislocations (Fig. 2c), needs vacancies to permanently move to dislocation cores from a surrounding material, while emission of vacancies (Fig. 2a) is not related to such a restrictive condition. As a corollary, emission of vacancies (Fig. 2a) occurs more intensively than absorption of vacancies (Fig. 2c) (and, more than that, than absorption of slow interstitial atoms; see Fig. 2d). With the aforesaid taken into account, in the following we will focus our consideration to the effects of only those processes of grain boundary dislocation climbing, that are related to emission of vacancies (Fig. 2a). The largest contribution to energy of “non-equilibrium” defect structures at grain boundaries (Fig. 1a) commonly is related to the existence of excess grain boundary dislocations. Therefore, climbing and annihilation of such dislocations, which are accompanied by emission of vacancies, are characteristic processes of relaxation of grain boundaries in nanocrystalline materials. Below, for definiteness, we will consider one of such processes, namely the climbing and consequent annihilation of two grain boundary dislocations that compose a dipole configuration of the vacancy type (that is, dipole of dislocations whose annihilation results in emission of vacancies); see Fig. 3. Stress fields of the grain boundary dislocations composing the dipole are effectively screened with the screening length  $\lambda$  being the dipole arm (distance between the dislocations; see Fig. 3a). Therefore, the energy  $W$  of the dislocation dipole, in the framework of linear theory of elasticity (e.g., [11, 15]), is given by the following approximate formula:



**Fig. 2.** Types of climbing of grain boundary dislocations.

$$W(\lambda) = 2W_d(\lambda) \approx \frac{Gb^2d}{2\pi(1-\nu)} \left( \ln \frac{\lambda}{r_0} + Z \right), \quad (3)$$

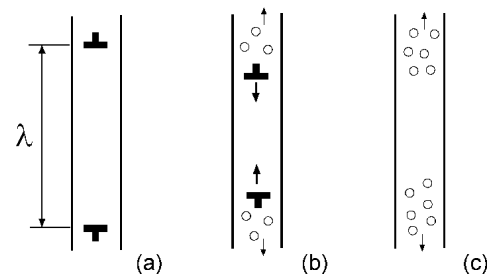
for  $\lambda > 2a$ . Here  $2W_d(\lambda)$  denotes the energy of a dislocation having  $\lambda$  as the screening length of its stress field,  $d$  the dislocation length,  $\pm b$  the dislocation Burgers vectors,  $G$  the shear modulus,  $\nu$  the Poisson ratio,  $r_0$  the dislocation core radius,  $Z$  the factor taking into account the contribution of the dislocation core into energy  $W$ .

The climbing of one of the dislocations composing the dipole configuration by  $a$ , the mean interatomic distance in the grain boundary (Figs. 3a and b), releases the dipole energy by value of  $\Delta W = W(\lambda) - W(\lambda - a)$  and results in emission of  $d/a$  vacancies. In this situation,  $\tilde{\epsilon}_f$ , the energy of formation of one vacancy at the climbing of the dislocations that compose the dipole configuration (Figs. 3a and b), is given as:

$$\tilde{\epsilon}_f = \epsilon_f - W_v(\lambda), \quad (4)$$

where  $\epsilon_f$  is the energy of formation of one vacancy in the grain boundary phase in the absence of dislocations, and  $W_v(\lambda)$  is the decrease of the dislocation dipole energy  $W$  due to emission of one vacancy, related to the climbing of the dislocations composing the dipole:

$$W_v(\lambda) = \frac{a}{d} \Delta W(\lambda) = \frac{a}{d} (W(\lambda) - W(\lambda - a)). \quad (5)$$



**Fig. 3.** Climbing and annihilation of grain boundary dislocations composing dipole configuration.

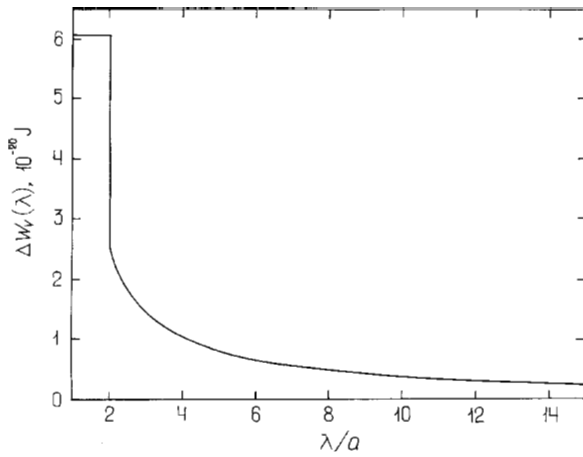


Fig. 4. Dependence of  $W_v$  on  $\lambda/a$ .

For  $\lambda > 2a$ , from (4) and (5) we find

$$W_v(\lambda) = \frac{Gb^2}{2\pi d(1-\nu)} \ln \frac{\lambda}{\lambda-a}. \quad (6)$$

For  $\lambda \leq 2a$ , stress fields of the dislocations composing the dipole configuration are localized in dislocation cores, in which case the dislocation energy is characterized by factor  $Z$ . The further climbing of the dislocation towards each other represents, in fact, the process of their annihilation resulting in emission of  $2(d/a)$  vacancies and decreasing the dipole energy from its value  $W(\lambda = 2a) \approx \frac{Gb^2 aZ}{2\pi(1-\nu)}$  at  $\lambda = 2a$  to zero that corresponds to  $\lambda = 0$  (annihilation). As a corollary, for  $\lambda \leq 2a$ , the dipole energy decreases by value of

$$W_v(\lambda) \approx \frac{Gb^2 aZ}{2\pi(1-\nu)} \quad (7)$$

due to emission of one vacancy. The dependence of  $W_v$  on  $\lambda/a$ , given by formulae (6) and (7), are shown in Fig. 4, for the following characteristic values of parameters:  $G = 50$  GPa,  $a \approx 0.3$  nm,  $b \approx a/3$ ,  $Z \approx 1$ , and  $\nu \approx 1/3$ . From Fig. 4 it follows that emission of vacancies is facilitated more intensively with decrease of the distance  $\lambda$  between the dislocations composing the dipole configuration.

Let us discuss the effect of dislocation-climb-induced emission of vacancies on diffusion in nanocrystalline materials. The coefficient of self-diffusion occurring via vacancy mechanism (which commonly is most effective) is given by formula (1), where factor  $\exp(-\varepsilon_f/kT)$  characterizes equilibrium concentration of vacancies, that is, the concentration of vacancies in the situation with dislocation climb and dilatation stresses do not influencing vacancy forma-

tion. Vacancy concentration in vicinity of the climbing dislocations (Fig. 3) is higher compared to the equilibrium concentration, because vacancy formation is facilitated due to the climbing of dislocations. The effect in question is quantitatively described by the following change of the vacancy formation energy:  $\varepsilon_f \rightarrow \tilde{\varepsilon}_f = \varepsilon_f - W_v^f$  and by the corresponding local change of diffusion coefficient:  $D \rightarrow D^*$ , where  $D^*$  in vicinity of the climbing dislocations (Fig. 3) is given as:

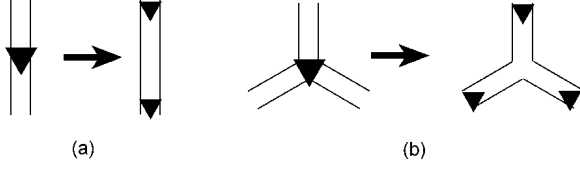
$$D^* = D \exp\left(\frac{W_v}{kT}\right). \quad (8)$$

With the dependence  $W_v(\lambda)$  (see Fig. 4) taken into consideration and factor  $\exp(\tilde{\varepsilon}_f/kT)$  averaged on  $\lambda$  (ranging from 0 to  $15a$ ), we find that self-diffusion coefficient in vicinity of the climbing dislocations is  $D^* \sim 3 \cdot 10^5 D$ .

The mean coefficient of self-diffusion in a solid with climbing dislocations (Fig. 3) is  $\tilde{D} \approx fD^* + (1-f)D$ , with  $f$  being the volume fraction of regions where dislocations climb. In nanocrystalline materials during relaxation period (after synthesis at highly non-equilibrium conditions) almost all grain boundaries contain non-equilibrium defect structures, in particular, "excess" dislocations whose annihilation enhances diffusion. In this situation, factor  $f$  is approximately equal to the volume fraction of the grain boundary phase in a nanocrystalline solid, that is,  $f \sim 0.1$  to  $0.5$ , depending on the mean grain size. As a corollary, we find  $\tilde{D} \approx fD^* + (1-f)D \approx (3$  to  $15) \cdot 10^4 D$ . This allows us to conclude that the climbing of grain boundary dislocations (Fig. 3) essentially enhances diffusion processes in nanocrystalline materials, causing increase of the self-diffusion coefficient by 4 or 5 orders.

#### 4. DILATATION STRESSES OF SPLIT DISCLINATIONS AT GRAIN BOUNDARIES AND DIFFUSION IN NANOCRYSTALLINE MATERIALS

Let us consider the effect of stress fields evolution, related to splitting of grain boundary disclinations on diffusion processes in nanocrystalline materials. Disclinations – line defects of the rotational type – are often formed at grain boundaries in nanocrystalline materials synthesized at highly non-equilibrium conditions (say, at high-pressure compaction of nanoparticles, ball milling, severe plastic deformation, etc.) [16,17]. Such disclinations are powerful sources of internal stresses in materials [17] and, therefore, undergo transformations that release their elastic energy density. In particular, grain boundary disclinations split into new disclinations (characterized by low values of strength, compared to pre-existent disclinations) [18, 19]



**Fig. 5.** Examples of splitting of grain boundary disclinations. (a) Linear splitting. (b) Triple splitting.

(see, e.g., Fig. 5), in which case the elastic energy density decreases and disclination-induced stress fields change.

The splitting of a grain boundary disclination, occurring in accordance with one of scenarios shown in Fig. 5, results in a dramatic change of the dilatation stress distribution in vicinity of the split disclination configuration in a nanocrystalline sample. In these circumstances, vacancies in vicinity of the split disclination configuration are affected by the aforesaid changes and move to regions where compressive stresses exist that are induced by the new disclinations (resulted from the splitting process). Migration of vacancies under action of the dilatation stresses induced by the new disclinations enhances the diffusion in vicinity of the split disclination configuration during some relaxation period.

Let us estimate the self-diffusion coefficient  $D_{loc}$  that characterizes local diffusion processes in vicinity of a split disclination configuration during relaxation period. As it is noted in section 2, the effect of the dilatation stresses on diffusion (occurring via vacancy migration), in the first approximation, is described by formula (1) with  $\varepsilon_f + \varepsilon_m$  being replaced by  $\varepsilon_f + \varepsilon_m + \varepsilon_{int}$  where  $\varepsilon_{int}$  in our case characterizes the elastic interaction between vacancies and dilatation stresses of new disclinations. As a corollary, the local diffusion coefficient is as follows:

$$D_{loc} \sim D \exp\left(-\frac{\varepsilon_{int}(x, y, z)}{kT}\right), \quad (9)$$

where the interaction energy  $\varepsilon_{int}$ , as given by formula (2), depends on dilatation stress fields  $\sigma_{xx}(x, y, z)$ ,  $\sigma_{yy}(x, y, z)$  and  $\sigma_{zz}(x, y, z)$  of the new disclinations.

In order to estimate  $D_{loc}$ , let us calculate dilatation stress fields in vicinity of the split disclination configurations shown in Fig. 5. Following [14], the stress fields of the disclinations can be written as follows:

$$\sigma_{xx} = \frac{\partial^2 \chi}{\partial x^2}, \quad \sigma_{yy} = \frac{\partial^2 \chi}{\partial y^2}, \quad \sigma_{zz} = \nu(\sigma_{xx} + \sigma_{yy}), \quad (10)$$

where

$$\chi = \frac{D\omega}{2} \left[ \left( (x-h)^2 + y^2 \right) \ln \frac{R^2 \left( (x-h)^2 + y^2 \right)}{(xh - R^2)^2 + y^2 h^2} + \frac{r^2 (h^2 - R^2)}{R^2} \right]. \quad (11)$$

Here  $R$  denotes the screening length of disclination stress fields, and  $2h$  the distance between disclinations. From formulae (10) and (11) we find the stresses of disclinations resulted from the linear splitting (Fig. 5a) to be given as:

$$\sigma_{xx} = \frac{4h^2}{R^2} + \sum_{i=1,2} \left[ 2 \ln \left( \frac{R^2 \alpha_i}{\beta_i} \right) + \frac{4\gamma_i^2}{\alpha_i} - \frac{(-1)^i 8h\gamma_i \delta_i}{\beta_i} - \frac{2h^2 (x^2 h^2 - \delta_i^2) \alpha_i}{\beta_i} \right], \quad (12)$$

$$\sigma_{yy} = \frac{4h^2}{R^2} + \sum_{i=1,2} \left[ 2 \ln \left( \frac{R^2 \alpha_i}{\beta_i} \right) + \frac{4x^2 (\beta_i - h^2 \alpha)^2}{\alpha_i \beta_i^2} \right], \quad (13)$$

$$\sigma_{zz} = \nu(\sigma_{xx} + \sigma_{yy}), \quad (14)$$

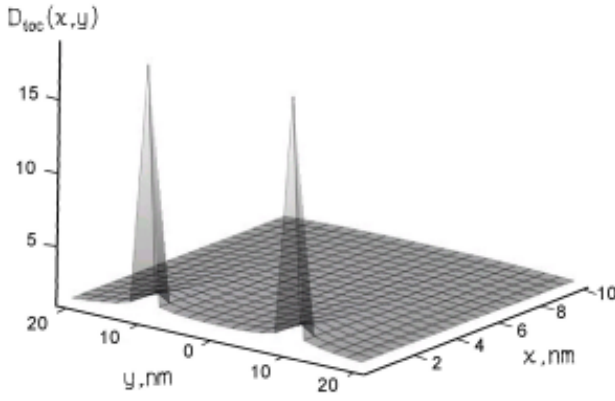
where  $i(=1,2)$  numerates the disclinations,  $\alpha_{1,2} = x^2 + (y \pm h)^2$ ,  $\beta_{1,2} = x^2 h^2 + (yh \pm R^2)^2$ ,  $\gamma_{1,2} = y \pm h$  and  $\delta_{1,2} = yh \pm R^2$ .

From formulae (2), (9), (12) and (13) we have the spatial distribution of  $D_{loc}(x, y)$  in vicinity of the split disclination configuration<sup>1</sup> (Fig. 5a) as shown in Fig. 6. With  $D_{loc}(x, y)$  averaged on spatial coordinates in vicinity of the disclination configuration resulted from the linear splitting (Fig. 5a), we find that the effect of dilatation stress evolution related to the linear splitting of grain boundary disclinations (Fig. 5a) leads to an increase of the diffusion coefficient by factor  $F_1 \approx 1.6$  during relaxation period. Here the factor is given as:

$$F_1 = \frac{1}{S} \int_S \exp\left[ (\sigma_{xx}(x, y) + \sigma_{yy}(x, y) + \sigma_{zz}(x, y)) \frac{\Delta V}{kT} \right] dx dy, \quad (15)$$

where  $S \approx (4h)^2$  is the area of the region in vicinity of the split disclination configuration shown in Fig. 5a. The mean coefficient of self-diffusion in a solid with split grain boundary disclinations (Fig. 5) is  $\tilde{D} \approx \tilde{f} F_{(1,2)} D + (1 - \tilde{f}) D$ , with  $\tilde{f}$  being the volume fraction of regions where disclinations split. In

<sup>1</sup> Disclinations shown in Fig. 5 have cores being parallel with axis  $z$ , in which case their characteristics under consideration are independent on coordinate  $z$ .



**Fig. 6.** Distribution of local diffusion coefficient  $D_{loc}(x,y)$  in vicinity of the disclination configuration resulted from a linear splitting.

nanocrystalline materials during a relaxation period (after synthesis at highly non-equilibrium conditions) most grain boundaries contain grain boundary disclinations. In this situation, factor  $\tilde{f}$  is close to the volume fraction of the grain boundary phase in a nanocrystalline solid, that is,  $\tilde{f}$  ranges tentatively from 0.1 to 0.5. As a corollary, we find  $\tilde{D} \approx (1.1 \text{ to } 1.3)D$ .

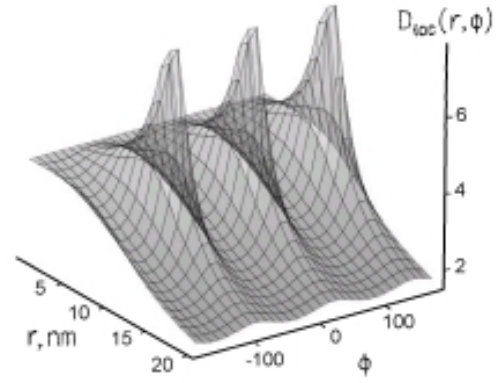
For disclinations resulted from the triple-line splitting (Fig. 5b), from formulae (10) and (11) we find the stresses as follows:

$$\sigma_{rr} = \sum_{\phi_i=30,150,270} \left[ \frac{2\tilde{h}^2}{R^2} + 2 \ln \frac{R^2 \xi_i}{\eta_i} + \frac{\rho_i^2}{\xi_i} - \frac{8\rho_i \kappa_i + 2r\tilde{h} \xi_i}{\eta_i} + \frac{4\tilde{h}^2 \xi_i^2}{\eta_i} \right], \quad (16)$$

$$\sigma_{\phi\phi} = \sum_{\phi_i=30,150,270} \left[ 2r\tilde{h} \cos(\phi - \phi_i) \left( 1 + \ln \frac{R^2 \xi_i}{\eta_i} \right) + \frac{4\tilde{h}^2 \sin^2(\phi - \phi_i)}{\xi_i} + \frac{4\tilde{h}^2 R^2 \sin^2(\phi - \phi_i) (R^2 - r^2) (\tilde{h}^2 - R^2)}{\eta_i^2} \right], \quad (17)$$

$$\sigma_{zz} = \nu(\sigma_{rr} + \sigma_{\phi\phi}), \quad (18)$$

where  $i (=1,2,3)$  numerates the new disclinations,  $(r,\phi)$  are the polar coordinates,  $\xi_i = r^2 + \tilde{h}^2 - 2r\tilde{h} \cos(\phi - \phi_i)$ ,  $\eta_i = R^2 + r^2 \tilde{h}^2 - 2Rr\tilde{h} \cos(\phi - \phi_i)$ ,  $\rho_i = r - \tilde{h} \cos(\phi - \phi_i)$ ,  $\kappa_i = r\tilde{h} - R \cos(\phi - \phi_i)$ ,  $\tilde{h}$  is the distance between the new disclinations,  $\phi_i (i=1,2,3)$  are the polar coordinates of grain boundary planes that form the triple junction (such planes are assumed to be misoriented by  $120^\circ$  relative to each other).



**Fig. 7.** Distribution of local diffusion coefficient  $D_{loc}(r,\phi)$  in vicinity of the disclination configuration resulted from a triple-line splitting.

From formulae (2) and (9) re-written in polar coordinates and (15) - (16), we have the spatial distribution of  $D_{loc}(r,\phi)$  in vicinity of the split disclination configuration (Fig. 5b) as shown in Fig. 7.

With  $D_{loc}(r,\phi)$  averaged on spatial coordinates in vicinity of the disclination configuration resulted from the triple splitting (Fig. 5b), we find that the effect of dilatation stress evolution related to the linear splitting of grain boundary disclinations (Fig. 5a) leads to an increase of the diffusion coefficient by factor  $F_i \sim 4.5$  during some relaxation period. Here the factor is given as:

$$F_i = \frac{1}{\tilde{S}} \int_{\tilde{S}} \exp \left[ (\sigma_{rr}(x,y) + \sigma_{\phi\phi}(x,y) + \sigma_{zz}(x,y)) \frac{\Delta V}{kT} \right] r dr d\phi, \quad (19)$$

where  $\tilde{S} \approx (4\tilde{h})^2$  is the area of the region in vicinity of the split disclination configuration shown in Fig. 5b.

The mean coefficient of self-diffusion in a solid with splitting grain boundary disclinations (Fig. 5) is  $\tilde{D} \approx \tilde{f} F_{(1,2)} D + (1 - \tilde{f}) D$ , with  $\tilde{f}$  being the volume fraction of regions where disclinations split. In nanocrystalline materials in relaxation period (after synthesis at highly non-equilibrium conditions) most grain boundaries contain grain boundary disclinations. In this situation, factor of the grain boundary phase in a nanocrystalline solid, that is,  $\tilde{f}$  ranges tentatively from 0.1 to 0.5. As a corollary, we find  $\tilde{D} \approx (1.35 \text{ to } 2.75)D$ .

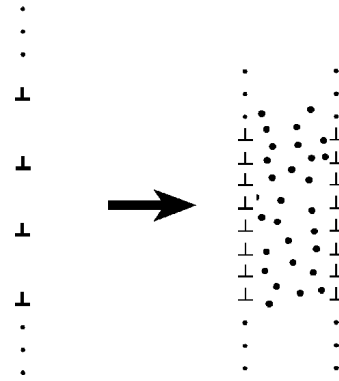
So, results of theoretical estimations made in this section allow us to conclude that the splitting transformations of grain boundary disclinations (Fig. 5) enhance self-diffusion processes in nanocrystalline materials. Due to this effect, the self-diffusion coefficient increases by tens per cent.

## 5. DILATATION STRESSES OF SPLIT DISLOCATIONS AT AMORPHOUS GRAIN BOUNDARIES AND DIFFUSION IN NANOCRYSTALLINE MATERIALS

The diffusion processes occurring in vicinities of amorphous grain boundaries are affected by stress fields created by boundary defects. Amorphous grain boundaries are frequently formed in sintered nanocrystalline and polycrystalline ceramics, influencing the macroscopic properties of such ceramics; see, e.g. [20-25]. The diffusional properties of nanocrystalline ceramics with amorphous grain boundaries are strongly affected by stress fields of boundary defects, which elastically interact with vacancies, basic carriers of diffusion. Following [26], fields of amorphous grain boundaries are effectively modeled as those induced by split grain boundary dislocations whose formation accompanies the formation of amorphous boundaries (Fig. 8). The effect of stress fields of amorphous grain boundaries on diffusion in nanocrystalline and polycrystalline materials has been theoretically examined in detail in paper [27]. In this section we will use quantitative results of work [27] in order to compare the influence of dislocation structures at amorphous grain boundaries (Fig. 8) on the self diffusion coefficient in nanocrystalline materials with that of defects previously examined in sections 3 and 4.

Following [26], transformation of a conventional tilt grain boundary into an amorphous grain boundary is associated with a re-arrangement of its grain boundary dislocation ensemble. In doing so, due to the fact that the amorphous disordered structures do not impose strict limitations on both spatial positions and Burgers vectors of grain boundary dislocations, such dislocations in a new, amorphous boundary are arranged in the way decreasing their elastic energy density. The discussed decrease of the elastic energy density causes the basic driving force  $F_{el}$  for the transformation of a conventional tilt boundary into an amorphous boundary. This force is calculated in the model [26] which to a first approximation describes the amorphous boundary to be of finite width,  $\lambda$ , with dislocation arrays at each of the interfaces between amorphous and the crystalline grain as shown in Fig. 8.

The elastic interaction between the diffusing species and boundary dislocations enhances diffusion in vicinities of amorphous grain boundaries. Following [27], the diffusion rate is increased by tens per cent in vicinities of amorphous grain boundaries due to the elastic interaction between point defects and split dislocation structures at amorphous boundaries. The effect discussed is essential in sintered nanocrystalline ceramics



**Fig. 8.** Transformation of conventional grain boundary containing grain boundary dislocations (left) into amorphous grain boundary (dotted region) with split boundary dislocations (right).

where the total volume fraction of the grain boundary phase is large and, as noted in [25], almost all high-angle boundaries are amorphized. Roughly speaking, this effect is of the same order as the effect of split disclinations on diffusion in nanocrystalline materials (see section 4). However, both these effects are negligible compared to that of climbing grain boundary dislocations (see section 3), which is capable of being responsible for experimentally observed (see [2, 6-9]) anomalously fast diffusion in nanocrystalline materials during some relaxation period after their synthesis at highly non-equilibrium conditions.

## 6. CONCLUDING REMARKS

Thus in this paper we have theoretically examined the effects of transformations of grain boundary defects on the diffusional properties of nanocrystalline materials. It is shown that the most significant effect is due to climbing of “excess” grain boundary disclinations formed at highly non-equilibrium conditions of synthesis of nanocrystalline materials. This effect causes the self diffusion coefficient to be increased by 4 to 5 orders in a nanocrystalline sample with grain boundaries containing “excess dislocations” (Fig. 1a) and, therefore, can be responsible for the experimentally observed anomalously fast diffusion in nanocrystalline materials.

Such transformations as splitting of grain boundary disclinations (Fig. 5) and dislocations (Fig. 8) also enhance diffusion processes in vicinity of grain boundaries with split defect configurations. However, their effects increase the self-diffusion coefficient by tens per cent and are negligible compared to that of the climbing of grain boundary dislocations.

In this paper we have focused on the effects of transformations of grain boundary defects on diffusion, that are related to emission of point defects as well as changes of dilatation stress fields of defects. In general,

however, there is also the effect related to low atomic density of grain boundary defect cores. Theoretical analysis of the role of grain boundary defect cores in diffusion processes in nanocrystalline materials will be the objective of further work.

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## REFERENCES

- [1] *Nanomaterials: Synthesis, Properties and Applications*, ed. by A.S.Edelstain and R.C.Cammarata (Institute of Physics Publ., Bristol and Philadelphia, 1996).
- [2] H. Gleiter // *Progr. Mater. Sci.* **33** (1989) 79.
- [3] *R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States.*, ed. by R.W.Siegel, E.Hu and M.C.Roco (International Technology Research Institute, Baltimore, 1997).
- [4] *Nanostructured Films and Coatings*, NATO ARW Ser., ed. by G.-M. Chow, I.A. Ovid'ko and T. Tsakalakos (Kluwer, Dordrecht, 2000).
- [5] *Nanotechnology Research Directions*, ed. by M.C. Roco, R.S. Williams and P. Alivisatos (Kluwer, Dordrecht, 2000).
- [6] H.-E. Schaefer, R. Wurschum, T. Gessmann, G. Stockl, P. Scharwaechter, W. Frank, R.Z. Valiev, H.-J.Fecht and C. Moelle // *Nanostruct. Mater.* **6** (1995) 869.
- [7] J. Horvath, R. Birringer and H. Gleiter // *Solid State Comm.* **62** (1987) 391.
- [8] Yu.R.Kolobov, G.P. Grabovetskaya, I.V. Ratochka and K.V. Ivanov // *Nanostruct. Mater* **12** (1999) 1127.
- [9] Yu.R. Kolobov, G.P. Grabovetskaya, K.V. Ivanov, R.Z. Valiev and T.C. Lowe, in: *Investigations and Applications of Severe Plastic Deformation*, NATO Science Ser., ed. by T.C. Lowe and R.Z. Valiev, (Kluwer, Dordrecht, 2000) p. 261.
- [10] H. Gleiter // *Nanostruct. Mater.* **6** (1995) 3.
- [11] V.I. Vladimirov, *Einfuhrung in die Physikalische Theorie der Plastizitat and Festigkeit* (Leipzig, VEB Deutscher Verlag fur Grundstoffindustrie, 1975).
- [12] L.A. Girifalco and D.O. Welch, *Point Defects and Diffusion in Strained Metals* (Gordon and Breach, 1967).
- [13] A.A. Nazarov, A.E. Romanov and R.Z. Valiev // *Nanostruct. Mater.* **4**, (1994) 93.
- [14] I.A. Ovid'ko, In: *Nanostructured Films and Coatings*, NATO ARW Ser. ed. by G.-M. Chow, I.A. Ovid'ko and T. Tsakalakos (Kluwer, Dordrecht, 2000) p. 231.
- [15] J.P. Hirth and J.Lothe, *Theory of Dislocations* (Mc Graw-Hill Publ. Co., NewYork, 1968).
- [16] V.G. Gryaznov, L.I. Trusov // *Progr. Mater. Sci.* **37** (1993) 289.
- [17] A.E. Romanov and V.I. Vladimirov , In: *Dislocations in Solids*, Vol. 9, ed. by F.R.N. Nabarro (Elsevier Science Publishers B.V., Amsterdam, 1992) p. 191.
- [18] M.Yu. Gutkin and I.A. Ovid'ko // *Phil. Mag. A* **70** (1994) 561.
- [19] M.Yu. Gutkin, K.N. Mikaelyan and I.A. Ovid'ko // *Phys. Stat. Sol. A* **153** (1996) 337.
- [20] Y. Kinemuchi, T. Yanai and K. Ishizaki // *Nanostr. Mater.* **9** (1997) 23.
- [21] X. Pan // *J. Am. Ceram. Soc.* **79** (1997) 2975.
- [22] H.Gu, X.Pan, I.Tanaka, R.M. Cannon, M.J. Hoffmann, H.Mullejans and M.Ruhle // *Mater. Sci. Forum* **207-209** (1996) 729.
- [23] X.Pan, M.Ruhle and T.Nihara // *Mater. Sci. Forum* **207-209** (1996) 761.
- [24] H.-J.Kleebe, G.Pezzotti and T.Nishida // *J. Mater. Sci. Lett.* **16** (1997) 453.
- [25] D.R. Clarke // *J. Am. Ceram. Soc.* **70** (1987) 15.
- [26] I.A. Ovid'ko and A.B. Reizis // *J. Phys. D* **32** (1999) 2833.
- [27] R.A. Masumura and I.A. Ovid'ko // *Mater. Phys. Mech.* **1** (2000) 31.