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Grain-boundary dislocations and enhanced diffusion in nanocrystalline bulk materials and films

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ABSTRACT

A theoretical model is suggested which describes the transformations of grain-boundary dislocation walls and their influence on diffusion processes in nanocrystalline materials fabricated under highly non-equilibrium conditions. It is shown that the decay of boundary dislocation walls of finite extent, occurring via the climb of boundary dislocations and the corresponding emission of vacancies, is capable of highly enhancing the grain-boundary diffusion in nanocrystalline materials. The enhanced diffusion, in turn, strongly affects the deformation behaviour of nanocrystalline materials. In the case of nanocrystalline films deposited on to substrates, the effects of misfit stresses on the transformations of boundary dislocation walls and the diffusion are analysed. It is demonstrated that the mean diffusion coefficient in a nanocrystalline film may increase by approximately several orders of magnitude owing to misfit stresses.

§ 1. INTRODUCTION

In recent years, nanocrystalline materials have attracted tremendous attention motivated by their wide applications in advanced technologies (for example Chow *et al.* (2000), Gleiter (2000) and Roco *et al.* (2000)). Of special interest, from both fundamental and applied viewpoints, are the specific peculiarities of diffusion in nanocrystalline materials which crucially affect their outstanding mechanical and sensing characteristics. Following Horvath *et al.* (1987), Gleiter (1989, 2000), Schaefer *et al.* (1995) and Kolobov *et al.* (1999, 2000), nanocrystalline materials exhibit anomalously enhanced diffusion properties. For instance, the boundary diffusion coefficients in bulk nanocrystalline materials fabricated by high-pressure compaction and severe plastic deformation methods are several orders of magnitude larger than those in conventional polycrystalline materials with the same chemical composition (Horvath *et al.* 1987, Gleiter 1989, 2000, Schaefer *et al.* 1995, Kolobov *et al.* 1999, 2000). With these experimental data, the anomalously fast diffusion is treated as one of the unique phenomena occurring in nanocrystalline materials owing to interface and nanoscale effects (Gleiter 1989). At the same time, however, there are experimental data indicating that the boundary diffusion coefficients in dense bulk nanocrystalline materials are lower than those measured by Horvath *et*

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al. (1987) and Schaefer *et al.* (1995), Kolobov *et al.* (1999, 2000) and similar to the boundary diffusion coefficients in conventional coarse-grained polycrystals or a little higher (Würschum *et al.* 1996, 1997, Tanimoto *et al.* 1999, 2000, Schaefer *et al.* 2000). These data form the basis of the viewpoint that the atomic diffusion in nanocrystalline materials is similar to that in conventional coarse-grained polycrystals. Thus, the difference between the diffusivities of nanocrystalline and coarse-grained materials is treated as related to only the difference between the volume fractions of the grain-boundary phase in these materials.

Thus, in general, there are controversial experimental data and theoretical representations on diffusion processes in nanocrystalline materials. Nevertheless, mechanically synthesized (by severe plastic deformation, etc.) nanocrystalline materials are definitely recognized to exhibit enhanced diffusion properties compared with those of nanocrystalline materials fabricated by non-mechanical (more equilibrium than mechanical) methods and those of coarse-grained polycrystals (Schaefer *et al.* 1995, Kolobov *et al.* 1999, 2000). This experimentally documented phenomenon can be naturally explained as occurring because of the deformation-induced, highly defected (non-equilibrium) state of grain boundaries, in which case the grain-boundary diffusivity significantly increases (Nazarov 2000, Ovid'ko and Reizis 2001). In particular, Ovid'ko and Reizis (2001) have shown that transformations of dipoles of grain-boundary dislocations (generated during synthesis of nanocrystalline specimens at highly non-equilibrium conditions) are capable of enhancing the mean diffusion coefficient by about two orders of magnitude in nanocrystalline materials. At the same time, as with grain-boundary dislocation dipoles, ragged dislocation walls terminated by grain boundary disclinations are intensively formed in fine-grained and nanocrystalline materials during their fabrication at highly non-equilibrium conditions (for example Valiev and Alexandrov (2000) and Murayama *et al.* (2002)). These defect configurations are considered to cause the rotational deformation mode in such materials (Gutkin *et al.* 2003b, Murayama *et al.* 2002, Ovid'ko 2002). In general, grain-boundary dislocation walls can also strongly affect the grain-boundary diffusion processes in nanocrystalline solids, in which case their effects should be definitely taken into account in the description of the experimentally documented enhancement of diffusion in mechanically synthesized nanocrystalline materials. The main aim of this paper is to examine theoretically the role of transformations of grain-boundary dislocation walls in the enhanced diffusion in nanocrystalline bulk materials and films.

§2. GRAIN-BOUNDARY DISLOCATIONS AND DIFFUSION ENHANCEMENT IN MECHANICALLY SYNTHESIZED NANOCRYSTALLINE MATERIALS: GENERAL ASPECTS

Let us discuss the effects of grain boundary dislocations on the diffusion behaviour of nanocrystalline materials in terms of the Arrhenius formula for diffusivity in solids. The coefficient D of self-diffusion occurring via transfer of vacancies† is given by the following Arrhenius relationship (for example Vladimirov (1975) and Sutton and Balluffi (1995)):

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† 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 (for example Vladimirov (1975) and Sutton and Balluffi (1995)).

$$D_0 = A \exp\left(-\frac{\varepsilon_\mathrm{f} + \varepsilon_\mathrm{m}}{kT}\right), \tag{1}$$

where A denotes the constant dependent on the parameters of the ideal crystalline lattice, k is the Boltzmann constant, T is the absolute temperature, and ε_f and ε_m are the energies of formation and migration respectively of vacancies. The basic carriers of self-diffusion processes in nanocrystalline materials (characterized by an extremely high volume fraction of the grain-boundary phase) are grain-boundary vacancies. Both the formation and the migration of boundary vacancies are highly sensitive to the dislocation structure of grain boundaries in nanocrystalline materials, in which case the diffusion coefficient depends on the structural and behavioural peculiarities of grain-boundary dislocations.

Highly defective grain boundaries are formed in mechanically synthesized nanocrystalline materials as well as in fine-grained polycrystals during superplastic deformation. Following Nazarov *et al.* (1993) and Valiev and Alexandrov (2000), such grain boundaries with high-density ensembles of deformation-induced or, in other words, non-equilibrium dislocations are called non-equilibrium grain boundaries. The density of non-equilibrium grain-boundary dislocations is a maximum in as-fabricated nanocrystalline specimens. During some relaxation time interval after fabrication, non-equilibrium dislocation structures at grain boundaries undergo transformations driven by a release of their elastic energy. More precisely, non-equilibrium dislocations move to new positions where they annihilate or form more ordered low-energy configurations. Following the theory of dislocations (Vladimirov 1975, Sutton and Balluffi 1995), climb of (grain boundary) dislocations is accompanied by the generation and absorption of point defects. We think that dislocation-climb-induced generation of new point defects (vacancies and interstitial atoms) serving as new extra carriers of diffusion gives rise to the essential enhancement of diffusion compared with diffusion at equilibrium conditions. Therefore, the generation of new extra vacancies occurs under the action of the driving force related to a release of the elastic energy of 'non-equilibrium' grain-boundary dislocations during their transformations. The action of the driving force essentially facilitates diffusion processes in nanocrystalline materials fabricated by mechanical methods. The effect discussed is quantitatively described by equation (1) with the sum $\varepsilon_\mathrm{f} + \varepsilon_\mathrm{m}$ being replaced by $\varepsilon_\mathrm{f} - \Delta W + \varepsilon_\mathrm{m}$, where ΔW (>0) is the energy release due to the climb of a grain-boundary dislocation, per one vacancy emitted by the dislocation.

Typical configurations of non-equilibrium grain-boundary dislocations in mechanically synthesized nanocrystalline materials are ragged-wall configurations (Valiev and Alexandrov 2000, Murayama *et al.* 2002) resulting, in particular, from dissociation of lattice dislocations entering the grain boundaries from grain interiors. The sessile boundary dislocations composing a ragged-wall configuration climb providing the spreading of the configuration (figure 1), which is driven by its elastic energy release. In the context of this paper, the climb of grain boundary dislocations forming the ragged wall is accompanied by the emission of extra (non-equilibrium) vacancies responsible for the diffusion enhancement. In the next two sections we shall calculate the energy related to the transformations of ragged dislocation wall, which enhance the diffusion processes in nanocrystalline bulk materials and films, and estimate the increase in the diffusion coefficient due to these transformations.

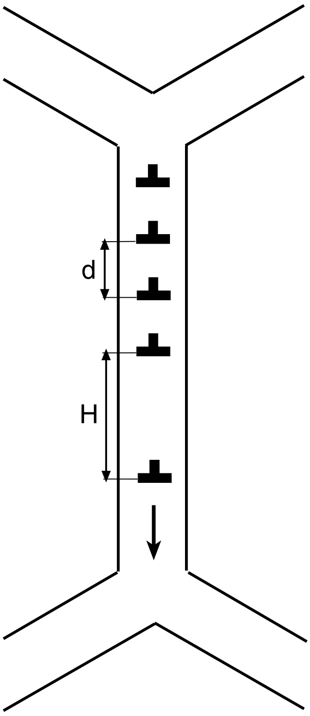

Figure 1. Ragged wall of periodically spaced (with period *d*) grain boundary dislocations. The lowest dislocation of the ragged wall climbs.

§ 3. TRANSFORMATIONS OF GRAIN-BOUNDARY DISLOCATION WALLS AND DIFFUSION IN BULK NANOCRYSTALLINE MATERIALS

Let us consider a grain-boundary dislocation wall of finite extent (a ragged dislocation wall) in a bulk nanocrystalline specimen (figure 1). The specimen is assumed to be an isotropic solid characterized by the shear modulus G and Poisson's ratio ν. The ragged wall consists of N grain-boundary dislocations assumed to be arranged periodically with interspacing d between the neighbouring dislocations. A nanocrystalline specimen fabricated under highly non-equilibrium conditions is characterized by a high density of defects distributed in a disordered manner that induce stress fields that are also distributed in a disorder manner. Because of this disorder, the stress fields of defects screen each other, in which case they are specified by some mean screening length R which is of the order of the characteristic length scale of structural inhomogeneities in nanocrystalline materials, that is about a few nanometres. With this taken into account, we suppose that the stress field of a ragged wall (figure 1) is screened at the length $R \approx 20$ nm. Therefore, for definiteness, we assume that the screening occurs owing to the stress field of another ragged dislocation wall of opposite sign distant by tentatively R from the initially considered wall configuration.

In general, as with other configurations of grain-boundary dislocations (for example Chisholm and Smith (1989), Tsu *et al.* (1998), Ovid'ko and Reizis (1999) and Gutkin and Ovid'ko (2001)), the ragged dislocation wall is capable of undergoing transformations driven by its elastic energy release. The elastic energy of a regular ragged wall consisting of N periodically spaced (with a period d) dislocations is proportional to $[(N-1)d]^2$. In these circumstances, a decrease in the number N of dislocations composing the ragged-wall configuration leads to its elastic energy release. As a corollary, after the ragged wall has been generated under highly non-equilibrium conditions of synthesis of a nanocrystalline specimen, it tends to decay during some relaxation time interval after the synthesis. Here we shall consider the decay of the ragged dislocation wall via consequent climb of grain-boundary dislocations of the wall configuration (towards another ragged dislocation wall consisting of grain boundary dislocations of opposite Burgers vectors).

The climb of grain-boundary dislocations during the relaxation time interval is accompanied by both emission and absorption of point defects: vacancies and interstitial atoms (figure 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 figure 2 (*a*)) is essentially more intensive than that of interstitial atoms (figure 2 (*b*)), because the formation energy of vacancies is essentially lower than the formation energy of interstitial atoms (Vladimirov 1975). Also, the absorption of vacancies and interstitial atoms, which accompanies the climb of grain-boundary dislocations (figures 2 (*c*) and (*d*)), needs vacancies and interstitial atoms respectively to move permanently to dislocation cores from a surrounding material, while the emission of vacancies (figure 2 (*a*)) is not related to such a strong restrictive condition. As a corollary, the emission of vacancies (figure 2 (*a*)) occurs more intensively than both the absorption of vacancies (figure 2 (*c*)) and the absorption of slow interstitial atoms (figure 2 (*d*)). With the aforesaid taken into account, in the following we shall focus on the effects of only those processes of grain-boundary dislocation climb that are accompanied by emission of vacancies (figure 2 (*a*)).

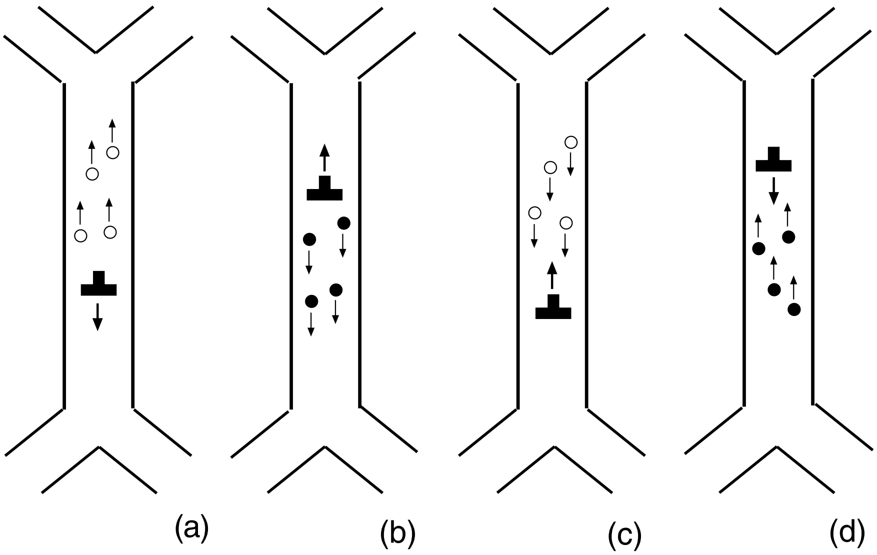

Figure 2. Types of grain-boundary dislocation climb.

In the situation discussed, the climb of the 'lowest' dislocation towards another dislocation wall (figure 1) is accompanied by emission of vacancies contributing to the diffusion enhancement. Let us examine the energy characteristics of the dislocation climb and the associated generation of vacancies. To simplify our analysis, we suppose that the 'lowest' dislocation of length l climbs, while other dislocations composing the ragged-wall configuration do not move. The energy W of the ragged wall with one climbing dislocation (figure 1) depends on the distance H between the climbing dislocation and the neighbouring stationary dislocation belonging to the ragged wall.

Let us consider an elementary climb of the lowest dislocation by a, where a is the mean interatomic distance in the grain boundary. The elementary climb releases the wall energy and results in emission of l/a vacancies. In this situation, $\tilde{\varepsilon}_{\mathrm{f}}$, the energy of formation of one vacancy at the climb of the dislocation, is given as

$$\tilde{\varepsilon}_{\mathrm{f}} = \varepsilon_{\mathrm{f}} - \Delta W. \tag{2}$$

Here ε_{f} is the energy of formation of one vacancy in the grain boundary phase in the absence of dislocations, and ΔW is the change of the dislocation wall energy due to emission of one vacancy, related to the climb of the lowest dislocation:

$$\Delta W(H) = [W^{\mathrm{int}}(H+a) - W^{\mathrm{int}}(H)]\,\frac{a}{l}. \tag{3}$$

Here $W^{\mathrm{int}}(H+a)$ and $W^{\mathrm{int}}(H)$ are the energies that characterize interaction between the stationary dislocations of the wall and the moving dislocation after and before respectively its elementary climb.

Let us number the dislocations of the ragged dislocation wall (figure 1) by integer i ranging from 0 to $N-1$, where the climbing dislocation has $i=0$, and the ith stationary dislocation (with $i=1,\ldots,N-1$) is distant by $H+(i-1)d$ from the climbing dislocation. Then, with $t=H+a$ and H, the energy $W^{\mathrm{int}}(t)$ can be represented in the form:

$$W^{\mathrm{int}}(t) = \sum_{i=1}^{N-1} W^{\mathrm{d-d}}(t,i), \tag{4}$$

where $W^{\mathrm{d-d}}(t,i)$ is the energy that characterizes interaction between the climbing dislocation and the ith stationary dislocation distant by $H+(i-1)d$ from the climbing dislocation. The energy $W^{\mathrm{d-d}}(t,i)$ (with $i=1,\ldots,N-1$) has been given by Hirth and Lothe (1982) as follows:

$$W^{\mathrm{d-d}}(t,i) = \frac{Gb^2 l}{2\pi(1-\nu)}\ln\left(\frac{R}{t+(i-1)d}\right), \tag{5}$$

where R denotes the screening length of the dislocation stress field and b is the magnitude of the dislocation Burgers vector. With equations (4) and (5) substituted into equation (3), we obtain:

$$\Delta W(H) = -\frac{Gb^2 a}{2\pi(1-\nu)}\sum_{i=0}^{N-2}\ln\left(\frac{H+a+id}{H+id}\right). \tag{6}$$

Thus, we have equation (6) for the energy ΔW that characterizes emission of a vacancy due to climb of a dislocation belonging to the ragged dislocation wall (figure 1). The local self-diffusion coefficient D^H near the climbing dislocation (distant by H from the nearest stationary dislocation of the ragged wall (figure 1)) is expressed through ΔW as (Ovid'ko and Reizis 2001) (see also discussion in § 2)

$$D^H = D_0 \exp\left(-\frac{\Delta W(H)}{kT}\right). \tag{7}$$

Here D_0 is the standard self-diffusion coefficient (given by equation (1)), that is the self-diffusion coefficient in the absence of vacancies emitted by the climbing dislocation; k is the Boltzmann constant and T is the absolute temperature.

Equations (6) and (7) allow us to estimate the increase in diffusion coefficient due to emission of vacancies by climbing dislocations (figure 1). To do this, let us introduce a parameter p, which is defined as follows. After the climbing dislocation has moved a distance p, it reaches the line where the driving force (a release of the elastic energy) for its climb approaches zero. The moving dislocation stops at this line, because further climb is energetically unfavourable. This means that, during the motion of the climbing dislocation (figure 1), the distance H between it and the nearest stationary dislocation of the ragged wall rises from d to $d+p$. In these circumstances, in order to estimate the diffusion coefficient in regions near climbing dislocations (similar to the dislocation shown in figure 1) in a nanocrystalline material during its relaxation time interval, it is necessary to average the value of $D^H = D_0 \exp[-\Delta W(H)/kT]$ over H ranging from d to $d+p$. In doing this, we find that the mean (in time) diffusion coefficient D of vacancy-rich regions near the climbing dislocations during the relaxation time period is given as

$$D = \frac{D_0}{p}\int_d^{d+p} \exp\left(-\frac{\Delta W(H)}{kT}\right) \mathrm{d}H. \tag{8}$$

(It is worth noting that the diffusion coefficient D is mean in time, but local in space.) For characteristic values of parameters, $G = 50\,\mathrm{GPa}$, $\nu = 1/3$, $T = 300\,\mathrm{K}$, $a = 0.3$–$0.4\,\mathrm{nm}$, $b = a/3$, $N = 5$, $d = 20$ b and $R = 20$ nm, from equations (6) and (8) it follows that $D = (2.8\text{–}21)D_0$. That is, vacancies emitted by climbing dislocations (figure 1) cause an essential enhancement in local diffusion. The local (in space) diffusion coefficient D given by equation (6) and (8) depends very strongly on both the mean interatomic spacing a and the shear modulus G. For example, an increase in a by one third results in a sevenfold rise in D.

The mean (in both time and material volume) coefficient of self-diffusion in a solid with grain boundary dislocation walls is

$$\langle D\rangle = FD + (1-F)D, \tag{9}$$

where F is the volume fraction of the vacancy-rich regions near the climbing dislocations. In a nanocrystalline material fabricated under highly non-equilibrium conditions, 'non-equilibrium' grain-boundary dislocations and their ragged walls exist in most grain boundaries when the material is in the as-fabricated state. Therefore, the factor F is close to the volume fraction of the grain-boundary phase. That is, F ranges from 0.1 to 0.5. As a result, we find that $\langle D\rangle = (1.8\text{–}11)D_0$. This in an agreement with experimental data (Schaefer *et al.* 1995, Kolobov *et al.* 1999, 2000), indicating the diffusion enhancement in mechanically synthesized nanocrystalline materials.

§4. INFLUENCE OF MISFIT STRESSES ON TRANSFORMATIONS OF GRAIN-BOUNDARY DISLOCATION STRUCTURES AND DIFFUSION PROCESSES IN NANOCRYSTALLINE FILMS

Let us consider the specific features of transformations of grain-boundary dislocation structures and diffusion processes in nanocrystalline films. In general, misfit stresses occurring as a result of mismatch between crystal lattice parameters of films and substrates strongly influence the structure and properties of solid films; for a review, see Fitzgerald (1991), van der Merwe (1991), Jain *et al.* (1997), Hirth (2000), Mahajan (2000) and Spaepen (2000). In particular, misfit stresses strongly affect transformations of grain-boundary dislocation structures in nanocrystalline and polycrystalline films (Ovid'ko 1999, 2001, Bobylev *et al.* 2001, Ovid'ko and Sheinerman 2001).

Let us examine the case where the grain boundary containing a ragged dislocation wall exists in a nanocrystalline film on a substrate (figure 3). Such walls of non-equilibrium grain-boundary dislocations can be intensively formed in nanocrystalline films and coatings fabricated under highly non-equilibrium conditions,

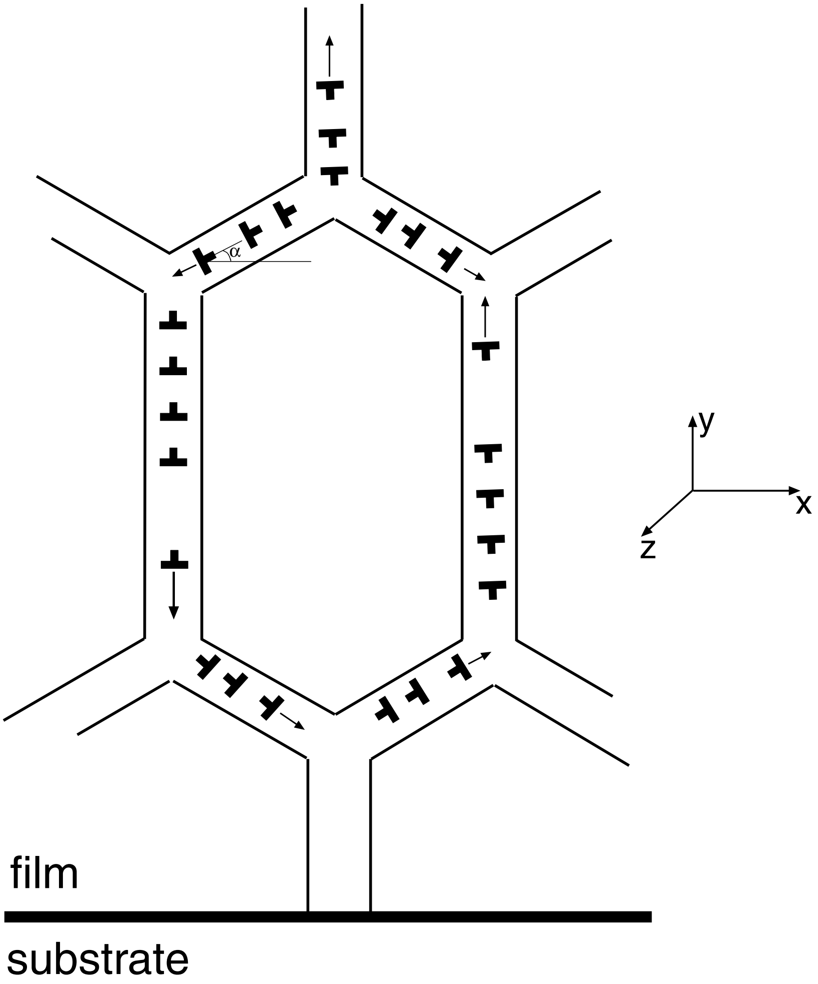

Figure 3. Grain-boundary dislocation walls in a nanocrystalline film.

for example, by a thermal spray method causing intensive plastic deformation of nanograins during their deposition on to a substrate. Let the dislocation Burgers vectors **b** make an angle α with the film–substrate interface. Also, let us assume that the dislocations composing the wall are located far enough from the free film surface. In these circumstances, the effect of the free surface on the dislocation stress field can be neglected. (This effect becomes negligibly small if the distance from the dislocation to the free surface exceeds the dislocation wall period $d = 20b$, that is, 2 nm in our case with the Burgers vector magnitude b of the grain-boundary dislocation equal to 0.1 nm.) In the framework of the model suggested, the film substrate boundary is characterized by a dilatation misfit $f = (a_s - a_f)/a_f$, where a_s and a_f are the crystal lattice parameters of the substrate and the film respectively. Owing to mismatch between these parameters, misfit stresses $\sigma^f_{xx} = \sigma^f_{zz} = [2G(1+\nu)/(1-\nu)]f$ exist in the film. The misfit stresses interact with climbing grain-boundary dislocations and thereby contribute to the self-diffusion coefficient of the nanocrystalline film.

Let us consider a ragged dislocation wall at a grain boundary and the climb of its 'lowest' dislocation, accompanied by emission of vacancies in a nanocrystalline film. The energy change ΔW^f (per one emitted vacancy) due to an elementary climb of the 'lowest' grain-boundary dislocation by the mean interatomic distance a in a grain boundary is as follows:

$$\Delta W^f = \Delta W + \frac{a}{l}\,\Delta W^{d-f}. \tag{10}$$

Here ΔW is the change of the self-energy of the dislocation wall due to the emission of one vacancy, given by equation (6), and ΔW^{d-f} is the change of the energy that characterizes interaction between the dislocation wall and the misfit stress field. The energy ΔW^{d-f} is equal to the difference between the energies that characterize the interaction of the 'lowest' dislocation with the misfit stress field after the elementary climb and prior to it, in which case we have:

$$\Delta W^{d\text{-}f} = \frac{2G(1+\nu)}{1-\nu}\,ablf\cos^2\alpha. \tag{11}$$

From equations (6), (10) and (11) we find that

$$\Delta W^f = -\frac{Gb^2a}{2\pi(1-\nu)}\left[\sum_{i=0}^{N-2}\ln\left(\frac{H+a+id}{H+id}\right) + \frac{4\pi(1+\nu)af\cos^2\alpha}{b}\right]. \tag{12}$$

As follows from equations (7), (10) and (11), the diffusion coefficient D^α_f in vacancy-rich regions of the film near the climbing dislocation is in the following relationship with the corresponding diffusion coefficient D in the bulk:

$$D^\alpha_f = D\exp(2c\cos^2\alpha). \tag{13}$$

Here α is the angle between the dislocation Burgers vector **b** and the film–substrate boundary, and

$$c = \frac{G(1+\nu)\,a^2\,bf}{(1-\nu)\,kT}. \tag{14}$$

In general, grain-boundary dislocation walls in the film and, therefore, their characteristic Burgers vectors are oriented at arbitrary angles relative to the film–substrate interface. In these circumstances, we should average the diffusion coefficient D_f^α (given by equation (13)) over angles α. In doing this, for definiteness, let us assume that the sum Burgers vector of the grain-boundary dislocations belonging to ragged dislocation walls is zero. That is, the ensemble the grain boundary dislocation walls does not accommodate the misfit stresses. In this situation, the diffusion coefficient D_f of the vacancy-rich regions near climbing dislocations is calculated by averaging D_f^α over α:

$$D_f = \frac{1}{2\pi}\int_{-\pi}^{\pi} D_f^\alpha \, d\alpha = De^c I_0(c). \qquad (15)$$

Here $I_0(z)$ is the modified Bessel function.

In general, grain-boundary dislocations can contribute to the accommodation of the misfit stresses (Ovid'ko 1999, 2001, Bobylev *et al.* 2001, Ovid'ko and Sheinerman 2001). In this case, the density of the grain-boundary dislocations with positive Burgers vector projections on the x axis ($b_x > 0$) parallel with the film–substrate boundary is different from the density of the grain boundary dislocations with $b_x < 0$. This means that we may distinguish the grain-boundary dislocations compensating for the misfit stresses from the set of all grain-boundary dislocations in a nanocrystalline film. The sum Burgers vector of the compensating dislocations has a non-zero x-projection b_x; such dislocations are characterized by either positive (in the case of $f > 0$) or negative (in the case of $f < 0$) value of b_x. As a corollary, these dislocations are characterized by Burgers vectors that make the angles α with the film–substrate boundary, randomly distributed within either the angle interval $-\pi/2 < \alpha < \pi/2$ (if $f > 0$) or the angle interval $\pi/2 < \alpha < 3\pi/2$ (if $f < 0$). As it follows from equation (11), the mean value of D_f^α for the compensating grain-boundary dislocations coincides with its mean value for the dislocations that do not contribute to relaxation of the misfit stresses. (This is because the climbing grain-boundary dislocations with opposite Burgers vectors climb in opposite directions and provide the same values of D_f^α.) Therefore, the presence of the compensating dislocations in the grain boundaries does not change D_f.

The mean diffusion coefficient $\langle D_f \rangle$ in an as-fabricated nanocrystalline film is calculated in the same way as that ($\langle D \rangle$) in a bulk nanocrystalline material (see § 3). Thus, we have $\langle D_f \rangle = FD_f + (1-F)D_f$, where F is the volume fraction of the grain-boundary phase. For definiteness, let us consider the situation with a positive f, where the energy ΔW^{d-f} is positive, and the misfit stresses give rise to an increase in the mean diffusion coefficient. In these circumstances, for $f = 0.01$ and characteristic values of parameters, given in § 3, we have $\langle D_f \rangle = (6.3\text{–}5.9 \times 10^4)D$. Thus, the misfit stresses strongly affect the climb of grain-boundary dislocations, in which case their effect may increase the mean diffusion coefficient in a nanocrystalline film by up to several orders of magnitude.

§ 5. CONCLUDING REMARKS

In this paper, the effect of the climb of grain boundary dislocation walls on the mean diffusion coefficient in nanocrystalline materials fabricated under highly non-equilibrium conditions (e.g. by ball milling and severe plastic deformation methods) has been theoretically examined. It has been shown that the diffusion in these materials is enhanced owing to intensive emission of non-equilibrium vacancies, which accompanies the dislocation climb. It is in agreement with experimental data (Schaefer *et al.* 1995, Kolobov *et al.* 1999, 2000), indicating the diffusion enhancement in mechanically synthesized nanocrystalline materials.

Following equations (6), (8) and (9) obtained in this paper, the diffusion coefficient of a nanocrystalline solid can vary in rather wide ranges depending on the interatomic spacing and elastic constants. For instance, the diffusion coefficient increases exponentially with increasing mean interatomic distance a in the grain-boundary phase. This parameter of a nanocrystalline material is sensitive to its fabrication technology. In general, highly non-equilibrium methods produce nanocrystalline materials with more disordered grain boundaries and larger interatomic distance a than weakly non-equilibrium methods do. The factor discussed contributes to the diffusion enhancement in mechanically synthesized nanocrystalline materials.

Also, in this paper it has been shown that the misfit stresses affect the climb of grain-boundary dislocations in nanocrystalline films. Owing to the effects of the misfit stresses, the mean diffusion coefficient in a nanocrystalline film may differ dramatically from that in the bulk. In particular, if the crystal lattice parameter of the substrate exceeds that of the film (the misfit f is positive), the mean diffusion coefficient in the nanocrystalline film may be several orders of magnitude higher than the diffusion coefficient of a nanocrystalline bulk material with the same chemical composition.

The results of our model are interesting in understanding the role of diffusion in plastic deformation processes in fine-grained materials. In particular, models (Masumura *et al.* 1998, Kim *et al.* 2000, Fedorov *et al.* 2002, Yamakov *et al.* 2002) based on the idea on the crucial contribution of grain-boundary diffusion to plastic flow of nanocrystalline materials should take into account enhancement of diffusion coefficient and its evolution in time, associated with transformations of grain boundary structures. Also, the low-temperature and high-strain-rate superplasticity (McFadden *et al.* 1999, Islamgaliev *et al.* 2001, Mukherjee 2002) of fine-grained and nanocrystalline materials fabricated by severe plastic deformation can be strongly influenced by boundary diffusion enhanced owing to transformations of grain-boundary dislocation structures. Therefore, grain-boundary junctions (exhibiting specific properties (King 1999)) can play a very essential role in the transformations and their effects on diffusion and plastic flow (for example, Fedorov *et al.* (2002, 2003)).

Also, the results obtained in this paper are worth taking into account in an analysis of experimental data (Weertman and Sanders 1994, Volpp *et al.* 1997) on different deformation behaviours exhibited by as-fabricated and heat-treated nanocrystalline materials. In particular, as has been experimentally detected by Weertman and Sanders (1994) and Volpp *et al.* (1997), the yield stress characterizing plastic flow of heat-treated nanocrystalline materials is essentially larger than that in the case of as-fabricated nanocrystalline materials with the same grain size. This experimentally documented fact is naturally explained in the context of our model, if grain boundary diffusion creep (Coble creep) dominates in plastically deformed nanocrystalline materials. In fact, with enhanced grain-boundary diffusion (conducted, in particular, by non-equilibrium vacancies generated owing to the climb of grain-boundary dislocations (figure 1)) in as-fabricated materials, Coble creep is enhanced in such materials compared with heat-treated nanocrystalline materials. As a result, as-fabricated nanocrystalline materials are softer than heat-treated materials.

Also, following Weertman and Sanders (1994) and Volpp *et al.* (1997), in the range of small grain sizes, heat-treated materials exhibit 'inverse' Hall–Petch behaviour (softening with reduction in grain size), while the yield stress or hardness of as-prepared materials slightly increases or saturates at grain sizes $d \leqslant 10\,\mathrm{nm}$ showing little or no 'inverse' Hall–Petch behaviour. It is difficult to explain directly this difference between the deformation behaviours of heat-treated and as-prepared nanocrystalline materials, using representations on Coble creep as the sole deformation mode. The idea of competition between Coble creep and the grain boundary sliding in the range of small grains is more effective in a description of the difference under consideration (Gutkin *et al.*, 2003a).

Finally, the results of the model elaborated in this paper are worth taking into consideration in an analysis of experimental data (Islamgaliev *et al.* 2001), indicating that heat treatment suppresses high-strain-rate superplasticity in nanocrystalline materials. A quantitative theoretical examination of the effects of diffusion processes on superplasticity in nanocrystalline materials will be the subject of future investigations of the present authors.

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