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**DEFECTS, DISLOCATIONS,
AND PHYSICS OF STRENGTH**

Grain-Boundary Dislocation Climb and Diffusion in Nanocrystalline Solids

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Abstract—The effect of grain-boundary dislocation transformations on diffusion in nanocrystalline solids is discussed. A theoretical model describing the enhancement of diffusion processes associated with the climb of grain-boundary dislocations in nanocrystalline solids is developed. © *2001 MAIK "Nauka/Interperiodica".*

The physical properties of nanocrystalline solids differ substantially from those of polycrystals of the same chemical composition (see, e.g., [1–10]). In particular, the nanocrystalline solids synthesized in strongly nonequilibrium conditions exhibit anomalously enhanced diffusion for at least a certain time after preparation [2, 9, 10]. For instance, the self-diffusion coefficient in nanocrystalline fcc materials exceeds by two to four orders of magnitude the grain-boundary diffusion coefficient in polycrystalline fcc materials of the same chemical composition [2, 9, 10].

According to [2], there are three factors that account for the enhanced diffusion in nanocrystalline solids: (1) Relaxation of grain-boundary structures, which occurs through relative grain displacements and reduces the free volume of grain-boundary structures, is impeded in nanocrystalline solids (this is due to the fact that the geometric conditions of relaxation of adjacent grain boundaries are usually poorly compatible because of the small nanocrystallite size). (2) In nanocrystalline solids, the volume fraction of triple grain-boundary junctions, where diffusion proceeds faster than in the "usual" grain boundaries, is extremely large. (3) The concentration of impurities which interfere frequently with grain-boundary diffusion is lower in nanocrystalline solids than in polycrystals.

However, the explanation put forward in [2] for the enhanced-diffusion phenomenon in nanocrystalline solids does not take into account the part played by grain-boundary dislocations in diffusion processes. At the same time, ensembles of grain-boundary dislocations are characterized by an extremely high density in nanocrystalline materials and strongly affect many physical properties of these materials (see, e.g., [11, 12]). The main objective of this work was to develop a theoretical model that would describe the effect of grain-boundary dislocation climb on diffusion processes in nanocrystalline solids.

1. GRAIN-BOUNDARY DISLOCATION TRANSFORMATIONS IN NANOCRYSTALLINE SOLIDS

Nanocrystalline solids are usually prepared under strongly nonequilibrium conditions (see, e.g., [1–5]). A nonequilibrium defect structure forms in the grain-boundary phase. In particular, the grain boundaries contain "excess" grain-boundary dislocations and, in addition, the geometrically necessary conditioned grain-boundary dislocations (i.e., dislocations that account for the misorientation of boundaries and which are associated with the structural geometry of the boundaries) are randomly displaced relative to their equilibrium spatial positions [11–13] (Fig. 1a). During a certain relaxation period after the synthesis of a nanocrystalline sample, the ensemble of grain-boundary dislocations undergoes transformations, which are accompanied by a decrease in its energy. The excess dislocations annihilate, and the geometrically neces-

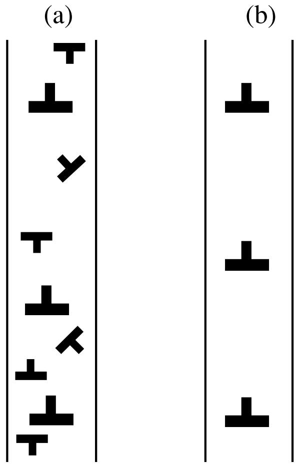

Fig. 1. Dislocation structure of (a) nonequilibrium and (b) equilibrium grain boundaries.

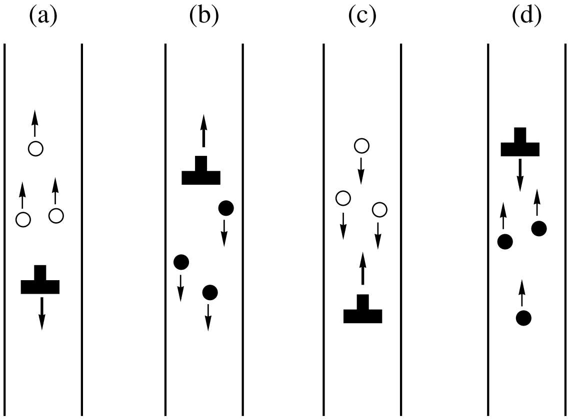

Fig. 2. Grain-boundary dislocation climb.

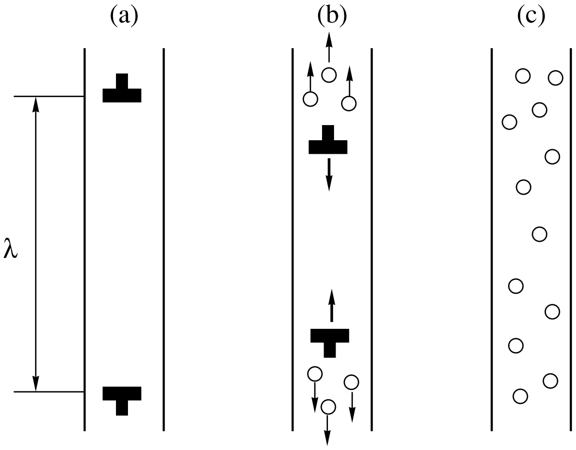

Fig. 3. Transformation of the grain-boundary dislocation dipole.

sary dislocations move to their "equilibrium" positions (Fig. 1b).

In our opinion, the grain-boundary dislocation transformations under study considerably affect the diffusion processes in nanocrystalline solids. Indeed, displacements of grain-boundary dislocations are accompanied by changes in their dilatation fields, which exert a noticeable effect on the migration of point defects, i.e., diffusion carriers, while the dislocation climb in grain boundaries is accompanied by the emission and absorption of point defects. The effect of the dilatation fields of grain-boundary dislocations on diffusion was studied in detail [14] for the case of transformation of such dislocations in the course of grain-boundary amorphization in nanocrystalline and polycrystalline solids. In the subsequent sections of this paper, we consider the effect of grain-boundary dislocation climb (as relaxation processes characteristic of grain-boundary structures) on vacancy emission and the corresponding diffusion enhancement in nanocrystalline solids.

2. VACANCY EMISSION IN THE CLIMB OF GRAIN-BOUNDARY DISLOCATIONS

The climb of grain-boundary dislocations is accompanied by the emission and absorption of vacancies and interstitials (Fig. 2). Note that because the mobility of vacancies is substantially higher than that of the interstitials [15], the emission of vacancies (the "detachment" of vacancies from the dislocation core and their subsequent migration into the adjacent grain-boundary phase, see Fig. 2a) is more intense than that of interstitial atoms (Fig. 2b). It should also be pointed out that the absorption of vacancies occurring in the course of the climb of a grain-boundary dislocation (Fig. 2c) requires a continuous vacancy supply from the surrounding material, whereas the emission of vacancies (Fig. 2a) is not impeded by such a restrictive requirement. Therefore, the emission of vacancies (Fig. 2a) proceeds at a higher rate than their absorption, Fig. 2c (the more so than that of the interstitials, Fig. 2d). In view of this, we restrict our subsequent analysis of the factors affecting diffusion to the grain-boundary dislocation climb processes that involve vacancy emission (Fig. 2a).

The major contribution to the energy of nonequilibrium defect structures in grain boundaries (Fig. 1a) usually results from the existence of excess grain-boundary dislocations. Therefore, the processes of climb and annihilation of such dislocations accompanied by vacancy emission are characteristic of the relaxation of grain-boundary structures in nanocrystalline solids. As an illustration, let us consider the climb and subsequent annihilation of two grain-boundary dislocations making up a vacancy-type dipole (Fig. 3).

Because the stress fields of the dislocations making up a dipole are screened efficiently with a screening radius λ (where λ is the dipole arm, see Fig. 3a), the energy *W* of this dislocation dipole is given in terms of the linear theory of dislocation elasticity [15, 16] by the approximate expression

$$W(\lambda) = 2W_d(\lambda) = \frac{Gb^2 d}{2\pi(1-\nu)}\left[\ln\left(\frac{\lambda}{r_0}\right) + z\right]. \qquad (1)$$

Here, $W_d(\lambda)$ is the energy of a dislocation characterized by the screening radius λ of its stress fields, *d* is the dislocation length, ±**b** are the Burgers vectors of the dislocations, *G* is the shear modulus, ν is the Poisson ratio, r_0 is the dislocation core radius, and *Z* is a factor taking into account the contribution of the dislocation core to the dislocation energy. The climb of a grain-boundary dislocation to an average interatomic distance *a* in the grain boundary (Figs. 3a, 3b) reduces the dipole energy by an amount $\Delta W = W(\lambda) - W(\lambda - a)$ and is accompanied by the emission of d/a vacancies. Therefore, the energy of formation of one vacancy involved in the climb of the dislocations making up the dipole (Figs. 3a, 3b) can be written as

$$\tilde{E}_v^f = E_v^f - W_v(\lambda), \quad (2)$$

where E_v^f is the energy of the vacancy formation in the dislocation-free grain-boundary phase and $W_v(\lambda)$ is the decrease in the dislocation dipole energy (Fig. 3a) caused by the emission of one vacancy:

$$W_v(\lambda) = \frac{a}{d}\Delta W(\lambda) \approx \frac{Gb^2 a}{2\pi(1-\nu)}\ln\left(\frac{\lambda}{\lambda - a}\right). \quad (3)$$

Equation (3) is valid for $\lambda > 2a$. For $\lambda \le 2a$, the stress fields of the dislocations making up the dipole are localized near the dislocation cores and the dislocation energy is determined by the factor Z. The climb of dislocations toward one another within the region of $\lambda \le 2a$ is essentially the process of dislocation annihilation, in which $2(d/a)$ vacancies are emitted and the dipole energy $W(\lambda = 2a) \approx \frac{Gb^2 dZ}{2\pi(1-\nu)}$ decreases to zero. As a consequence, for $\lambda \le 2a$, the energy of the dipole of annihilating dislocations decreases on the emission of one vacancy by an amount

$$W_v(\lambda) = \frac{a}{2d}W(\lambda = 2a) \approx \frac{Gb^2 aZ}{\pi(1-\nu)}. \quad (4)$$

The dependence of W_v on λ/a given by Eqs. (3) and (4) is plotted in Fig. 4 within the region of λ from 0 to $15a$ for the following characteristic values of the parameters: $G = 50$ GPa, $a \approx 0.3$ nm, $b \approx a/3$, $Z \approx 1$, and $\nu \approx 1/3$. The shape of this relation shows that the vacancy emission is facilitated when the dislocations making up the dipole approach each other.

3. EFFECT OF GRAIN-BOUNDARY DISLOCATION CLIMB ON THE DIFFUSION COEFFICIENT

The coefficient of diffusion occurring via the vacancy mechanism (which is usually the most efficient mechanism) is given by the relation (see, e.g., [15])

$$D = D_0 \exp(-E_v^m/kT)\exp(-E_v^f/kT), \quad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, D_0 is a constant, and E_v^m is the activation energy for the vacancy migration. The factor $\exp(-E_v^f/kT)$ in Eq. (5) characterizes the equilibrium concentration of vacancies (as the main diffusion carriers) in a solid when the influence of defect transformations and dilatation fields on diffusion is ignored. In the vicinity of climbing dislocations (Fig. 3), the vacancy concentration exceeds the equilibrium concentration, because the vacancies are produced here in more favorable conditions. This effect is characterized quantitatively by the change in energy for the vacancy formation $E_v^f \longrightarrow \tilde{E}_v^f = E_v^f - W_v$ and by the corresponding local change in the diffusion coefficient $D \longrightarrow D^*$, where D^* in the vicinity of climbing grain-boundary dislocations (Fig. 3) can be written as

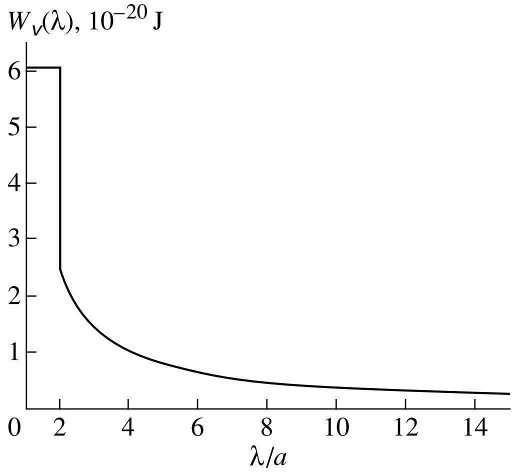

Fig. 4. W_v vs. λ/a relation.

$$\begin{aligned} D^* &= D_0 \exp(-E_v^m/kT)\exp(-(E_v^f - W_v)/kT) \\ &= D\exp(W_v/kT). \end{aligned} \quad (6)$$

Using the $W_v(\lambda)$ relation (Fig. 4) and averaging the factor $\exp(W_v/kT)$ over λ within the λ interval from 0 to $15a$, we find that in the vicinity of climbing dislocations (Fig. 3), the diffusion coefficient is $D^* \approx 3 \times 10^5 D$.

The average diffusion coefficient in a solid with climbing grain-boundary dislocations is $\tilde{D} \approx fD^*$, where f is the fraction of the regions with the climb. In nanocrystalline solids, during the relaxation period (after their preparation in strongly nonequilibrium conditions), practically all grain boundaries contain nonequilibrium defect structures, in particular, excess dislocations, whose climb enhances diffusion. In this case, the coefficient f is approximately equal to the volume fraction of the grain-boundary phase; i.e., $f \approx 0.1$–0.5, depending on the average grain size in the nanocrystalline solid. Therefore, we have $\tilde{D} \approx fD^* \approx (3\text{–}15) \times 10^4 D$. Thus, during the relaxation of grain-boundary structures, the climb of grain-boundary dislocations (Fig. 3) substantially enhances the diffusion processes, which is manifest in the average diffusion coefficient changing by four to five orders of magnitude.

To sum up, the macroscopic properties of nanocrystalline solids depend noticeably on the properties of grain boundaries. In particular, grain-boundary dislocation transformations are capable of appreciably affecting the diffusion characteristics of nanocrystalline solids. The theoretical analysis carried out in this work suggests that the climb of grain-boundary dislocations making up dipoles (Fig. 3) is accompanied by intense emission of vacancies, which enhances the diffusion in nanocrystalline solids by several orders of magnitude. The theoretical estimates obtained are in satisfactory agreement with experimental data on the diffusion properties of fcc nanocrystalline materials [2, 9, 10].

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