Size effects of dislocation stability in nanocrystals

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In this paper the size effect of lattice-dislocation stability in nanocrystals (NC's) caused by a strong interaction of dislocations with interfaces is analyzed. When the nanocrystallite size l becomes less than the characteristic length Λ, a substantial dislocation redistribution in the nanocrystal may occur. This length is estimated to be dozens of nanometers and depends on the character of interfaces: coherent or incoherent (slipping), on a difference of elastic moduli of NC phases, etc. Simple analytical estimations of Λ on the basis of exact calculations have been obtained.

INTRODUCTION

When the dimensions of solids are comparable with the correlation length of some physical phenomena (e.g., the Cooper-pair length, an exciton size, a dislocation pileup length, etc.), a detailed revision of all physical properties of solids becomes necessary, usually referred to as size effects. Size effects may also occur for structural elements of massive solids (crystallites, pores, etc.).

When the size of crystallites is very small (of the order of nanometers), most physical properties of the polycrystals should suffer a noticeable change. Usually such polycrystals are called nanocrystals (NC's) (see, for example, Ref. 1).

Mechanical properties of solids are, in most cases, structure sensitive, so an influence of size effects on the behavior of lattice defects in crystals ought to drastically change their physicomechanical characteristics. One of the most important crystal defects determining mechanical properties are lattice dislocations.

For individual small crystals, as were shown earlier,[2] lattice dislocations tend to leave the crystals when the crystal size is less than the characteristic length

$$\Lambda_p \simeq Gb/\sigma_p \simeq 10^1-10^2 \text{ nm} .$$

Here G is the shear modulus, b is the Burgers vector of the dislocation, and σ_p is the Peierls or friction stress. In the case of NC's (especially in the case of heterogeneous ones), the dislocation behavior is much more complicated. This paper presents a theoretical analysis of the problem of lattice dislocation stability in NC's.

RESULTS

Situations realized for dislocations in NC's may be considered as intermediate between several cases with the idealized dislocation geometry and crystallite shape. Here two model situations are analyzed: a prismatic circular dislocation loop axially arranged in a spherical crystallite, and a straight-line edge dislocation parallel to the axis of an infinite cylinder (see Fig. 1).

The elastic properties of a real NC are taken into account as follows: the nanocrystallite has the isotropic elastic moduli $G^{(1)},v^{(1)}$, where $G^{(1)}$ is the shear modulus of the nanocrystallite and $v^{(1)}$ is its Poisson's ratio. The effective matrix around the nanocrystallite has the elastic moduli $G^{(m)},v^{(m)}=v^{(1)}=v$; $G^{(m)}$ is estimated by means of the rule of the mechanical mixture:[3]

$$G^{(m)}=\sum_{i=1}^{N} f_i G^{(i)} ,$$

here f_i are the volume fractions of NC constituents. The state of the NC interfaces may be described by two different models—a coherent boundary (the intercrystallite sliding is constrained) and a slipping boundary (sliding may be provided by the high mobility of grain boundary structures, particularly at high temperatures; such a boundary does not transmit shear stresses).

A mathematical formulation of the boundary conditions is described in the following.

(1) A coherent boundary: $U_i^{(1)}|_s=U_i^{(m)}|_s$, $\sigma_{ni}^{(1)}|_s=\sigma_{ni}^{(m)}|s$. Here $i=1-3$, the index n corresponds to the normal to the interface s, indices (1) and (m) denote the elastic fields in the considered nanocrystallite and in the isotropic matrix, correspondingly, and U_i and σ_{ij} are displacement and stress tensor components, respectively.

(2) A slipping interface: $U_n^{(1)}|_s=U_n^{(m)}|_s$, $\sigma_{nn}^{(1)}|_s=\sigma_{nn}^{(m)}|_s$, $\sigma_{nj}^{(1,m)}|_s=0$, $j\neq n$.

For an arbitrary lattice defect in a nanocrystallite, the elastic fields may be represented by the sum[4] $\sigma_{ij}^{(k)\infty}+\sigma_{ij}^{(k)im}$, $k=1,m$. The first term stands for the stresses generated by the defect in an infinite solid. The

second one corresponds to "image" stress fields providing the fulfillment of the boundary conditions written above.

For the analysis of the dislocation stability in NC's, it is necessary to evaluate the force that affected a dislocation inside the nanocrystallite. This force corresponds to the image stresses $\sigma_{ij}^{(k)im}$.[5] For the geometries illustrated by Fig. 1, the force component (per unit dislocation length) acting in its glide plane is as follows: $F_z = b_z \sigma_{\rho z}^{(1)im}$ for the model of the sphere [Fig. 1(a)] and $F_x = b_x \sigma_{xy}^{(1)im}$ for the model of the cylinder [Fig. 1(b)]. Here b_z and b_x are the magnitudes of the Burgers vector of the prismatic dislocation loop and the edge dislocation, correspondingly.

In the case of the cylinder with a coherent interface, the simple formula for the image force obtained in the paper[5] has been used in our analysis. In the case of the cylinder with the slipping interface, the boundary problem has recently been exactly solved[6] by means of the Kolosov-Muskhelishvili method.[7] The image stress for the present case has the following form:

$$\sigma_{xy}^{(1)im} = G^{(m)}G^{(1)}(G^{(m)}+G^{(1)})^{-1}[2\pi(1-\upsilon)^2]^{-1}(b_x/a)$$
$$\times p\cos\varphi\{\sin\varphi[\Phi(\eta,p^2)p^{-2}(s_1p^4+s_2p^2+s_3)+s_4/(1-p^2)+s_5p^2+s_6)]$$
$$+\cos\varphi[\Phi(\eta,p^2)p^{-2}(s_7p^4+s_8p^2+s_9)+s_{10}/(1-p^2)+s_{11}p^2+s_{12}]\}\ ,$$
$$\eta=[G^{(1)}(3+4\upsilon)+G^{(m)}]/[2(1-\upsilon)(G^{(1)}+G^{(m)})]\ . \tag{1}$$

Here $p=\rho/a$ [see Fig. 1(b)], $\Phi(\eta,p^2)$ is the hypergeometrical function

$$\Phi(x,y)=\sum_{n=1}^{\infty} y^n(n+x)^{-1}\ ,$$

and s_i are cumbersome combinations of elastic moduli.

One should note that an analogous inverse problem for the case of a cylindrical inclusion and an edge dislocation near the latter was analyzed in detail in Ref. 8.

The force F_z for the model of the sphere and both types of interfaces has been obtained by means of a method developed in Ref. 9. (For details of the derivations of image forces F_x and F_z, see Ref. 6.)

To analyze the stability of glissile dislocations in NC's, the obtained elastic forces should be compared with the friction forces acting on a dislocation in the crystal lattice. As a rule, the Peierls stress σ_p gives a dominant contribution in dislocation friction processes. It is useful to introduce two parameters characterizing the dislocation stability in NC's. The first one, $\Delta = V_e/V$, is the relative volume of dislocation equilibrium, where V is a nanocrystallite total volume and V_e is a volume of the region of the dislocation equilibrium in this nanocrystallite, corresponding to the fulfillment of the condition

$$-b_{x,z}\sigma_p < F_{x,z} < b_{x,z}\sigma_p\ .$$

The second parameter is the characteristic length Λ defined here as the radius of the cylindrical or spherical nanocrystallite having $\Delta=\frac{1}{2}$. Thus, Λ can be called the characteristic size of the dislocation stability. Exact dependencies of Δ and Λ on the NC characteristics are very awkward; therefore, here they are represented graphically by Figs. 2 and 3.

It is worth mentioning that, when the effective elastic moduli of the external matrix are substantially less than the elastic moduli of the nanocrystallite, the behavior of the dislocations is similar to their behavior in the case of

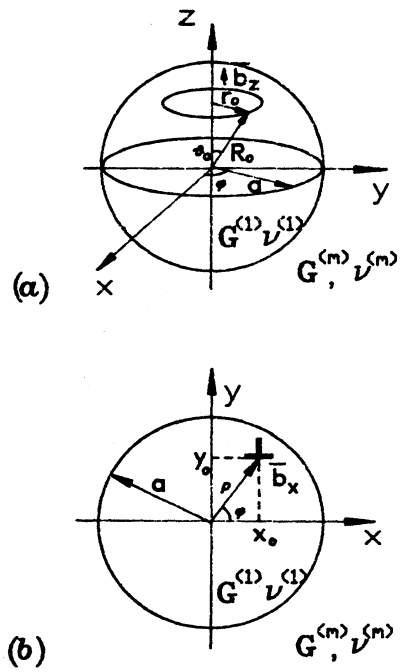

FIG. 1. Models of nanocrystallites containing dislocations. (a) A prismatic circular dislocation loop with the Burgers vector b_z in an elastic isotropic sphere having elastic moduli $G^{(1)},\upsilon^{(1)}$ and located in an effective matrix having elastic moduli $G^{(m)},\upsilon^{(m)}$. (b) A straight-line edge dislocation with the Burgers vector b_x in an elastic isotropic cylinder with elastic moduli $G^{(1)},\upsilon^{(1)}$ and located in an effective matrix with moduli $G^{(m)},\upsilon^{(m)}$.

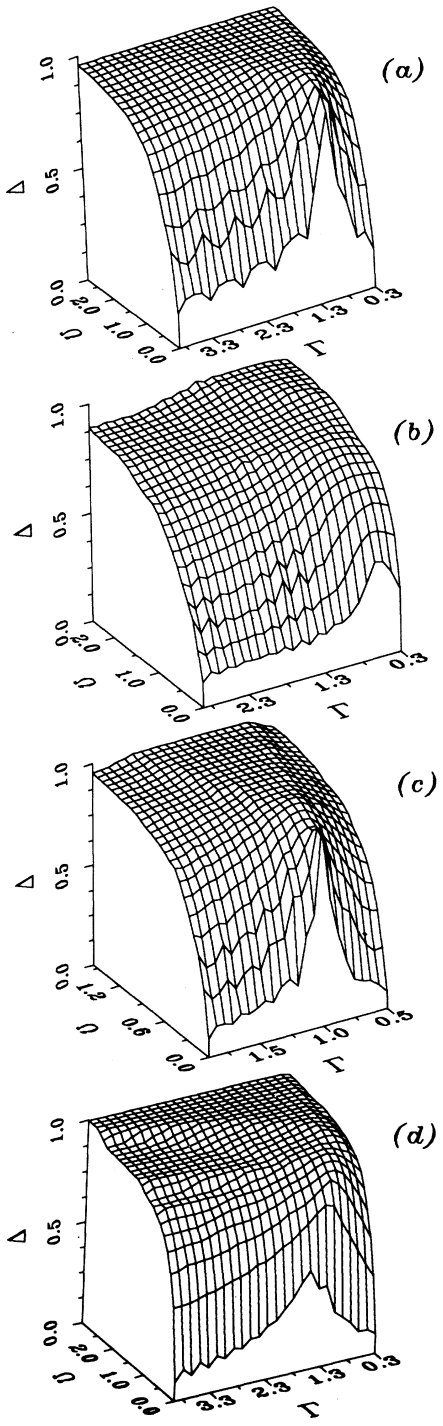

FIG. 2. Relative volume Δ of the dislocation equilibrium in a nanocrystallite in dependence on the parameter $\Omega=2l\sigma_p/G^{(1)}b$, characterizing the nanocrystallite size and its material, and the elastic modulus ratio $\Gamma=G^{(1)}/G^{(m)}$. (a) A spherical nanocrystallite with a coherent boundary, (b) a spherical one with a slipping boundary, (c) a cylindrical nanocrystallite with a coherent boundary, and (d) a cylindrical one with a slipping boundary.

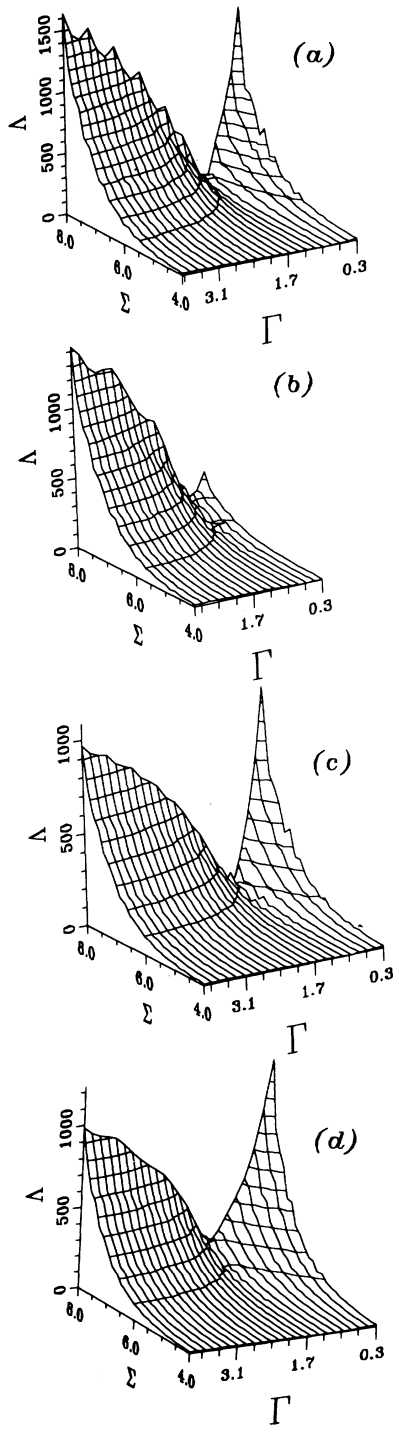

FIG. 3. The dependence of the characteristic length of dislocation stability in nanocrystallites Λ on the parameter $\Sigma=2\log_{10}(G^{(1)}/\sigma_p)$ and the ratio of the elastic moduli $\Gamma=G^{(1)}/G^{(m)}$. (a) A spherical nanocrystallite with a coherent boundary, (b) a spherical one with a slipping boundary, (c) a cylindrical nanocrystallite with a coherent boundary, and (d) a cylindrical one with a slipping boundary.

free nanoparticles.[2] However, for screw dislocations, an additional factor of stability, provided by the Eshelby torsion, may arise.[10]

DISCUSSION

Generally speaking, dislocations are thermodynamically non-equilibrium (metastable) objects. Their presence in crystals is provided by the friction forces constraining the dislocation exit from crystals. When the interaction of dislocations with polycrystal interfaces in NC's becomes comparable with the Peierls force, an essential dislocation redistribution should occur. In particular, these regions in nanocrystallites can appear from where glissile dislocations are being expelled.

Figure 2 displays the dependence of the relative volume of dislocation equilibrium Δ on the crystallite size l, the Peierls stress σ_p, and the elastic modulus ratio $\Gamma=G^{(1)}/G^{(m)}$. One can see from this figure that Δ decreases with l; it has an especially steep change when l is less than $\sim G^{(1)}b/\sigma_p$. This dependence expresses the size effect of dislocation stability. Besides, Δ nonmonotonously alters with Γ; although, in the case of nanocrystallites with slipping boundaries, this tendency is less pronounced. An accurate analysis of the tensile stresses shows that they are caused by the following effect: the image force $F_{x,z}$ changes its sign in the crystallite volume even when $\Gamma=1$ for these boundary conditions. Thus, in this case one may introduce three conventional regions: a region of a dislocation equilibrium ($-b_{x,z}\sigma_p<F_{x,z}<b_{x,z}\sigma_p$), a region of a dislocation expelling ($F_{x,z}>b_{x,z}\sigma_p$), and a region from where dislocations are being removed to the first one ($F_{x,z}<-b_{x,z}\sigma_p$). Incoherency of the interface means that the crystallite is less sensitive to the elastic-field features of its matrix (one may imagine that atomic bindings across the interface are cut) in comparison with the case of the coherent boundary conditions. Thus, volumes of the regions alter less noticeably with a change of elastic moduli Γ than in the latter case.

It is clear for the coherent boundary [see Figs. 2(a) and 2(c)] that dislocations in crystallites are absolutely stable when $\Gamma=1$ as one may expect (small deflections from the strict equality V_e to V at $\Gamma=1$ is caused by the numerical averaging procedure).

As follows from the definition of Λ that the above-described size effect of the dislocation stability in NC's takes place when $l<\Lambda$. The dependence of the characteristic length Λ on σ_p and Γ is presented in Fig. 3. Λ is always inversely proportional to the Peierls stress σ_p as it follows from the equality of the Peierls stress σ_p and the image stress which is proportional to $G^{(1)}b/l$. An important feature of all the dependencies is the presence of a peculiar fold. In other words, there exists such a value Γ_c of the ratio Γ that the size effect becomes very weak (or disappears at all in the case of coherent boundaries [Figs. 3(a) and 3(c)]. For coherent boundaries the critical ratio Γ_c is equal to 1 for any geometry, while in the case of slipping boundaries $\Gamma_c\approx 0.6$ for the geometry illustrated by Fig. 1(a) and $\Gamma_c\approx 1.4$ in another case [Fig. 1(b)]. When $\Gamma>\Gamma_c$, the dislocations are expelled from the NC and the dislocation density decreases; when $\Gamma<\Gamma_c$, the opposite situation takes place.

In a number of physically important situations, one may assume that $G^{(1)}\approx G^{(m)}$ (as in case of homogeneous NC's) and obtain the following approximation:

$$\Lambda=[\theta_0+\theta_1(\Gamma-1)]Gb/\sigma_p \ . \tag{2}$$

Here $\theta_0=0$, $\theta_1\approx 0.1\,\mathrm{sgn}(\Gamma-1)$ for the sphere with a coherent boundary; $\theta_0=0.06$, $\theta_1\approx 0.17$ for the sphere with a slipping boundary; $\theta_0=0$, $\theta_1\approx 0.08\,\mathrm{sgn}(\Gamma-1)$ for the cylinder with a coherent boundary, and $\theta_0\approx 0.04$, $\theta_1\approx -0.05$ for the cylinder with a slipping boundary.

The parameter Λ corresponds to a dramatic change of lattice dislocation density in NC's and can be measured experimentally. Theoretically predicted values of Λ for some homogeneous metal NC's with slipping boundaries are presented in Table I.

In reality, the magnitude of Λ should be somewhat higher since dislocations may be bound with boundaries with stacking faults or may intersect the boundaries, etc. In the first case, an additional force proportional to γ attracts partial dislocations to the interface (where γ is the specific energy of the stacking fault). In the second case, the presence of a conjugated boundary step gives an additional force proportional to $G^{(1)}b^2/l$ stimulating the dislocation exit from the nanocrystallite. For an arbitrary geometry one should also take into account the effect of the shortening of the dislocation length. These forces may intensify the process of the dislocation redistribution.

One should mention that, in the case of precipitations of ordered alloys constituting nanocrystals, the antiphase

TABLE I. Characteristic length Λ of dislocation stability for metal nanocrystals with slipping interfaces. The data for σ_p, $G^{(1)}$, and b can be found in Refs. 2 and 4.

	Cu	Al	Ni	α-Fe
G (GPa)	33	28	95	85
b (nm)	0.256	0.286	0.249	0.248
σ_p, (10^{-2} GPa)	1.67	6.56	8.7	45.5
Λ (nm), sphere	38	18	16	3
Λ (nm), cylinder	24	11	10	2

boundaries may play the same role as the stacking faults discussed above. The antiphase boundary energy, as a rule, is two or three times more than the stacking fault energy (for instance, in the Cu_3Au, see Ref. 11), thus the considered interaction must be more intensive.

The reasons considered above show that, if the condition $l < \Lambda$ is fulfilled, all glissile dislocations in elastically stiffer phases of heterogeneous NC's will come to the interfaces in some time, while in elastically softer phases, dislocations will be confined in the central part of the nanocrystallites.

For aged NC's with $l < \Lambda$, internal stresses may appreciably relax due to dislocation redistribution. Plastic shear in such NC's should be localized near the interfaces.

CONCLUSIONS

(1) When the size of the grains in nanocrystals becomes less than the characteristic length Λ, the dislocation arrangement and density drastically change. This effect can occur even for homogeneous nanocrystals having mobile boundary structures (slipping boundaries). Glissile dislocations are predominantly arranged near interfaces. (2) There exists such a value Γ_c of the elastic modulus ratio Γ for a heterophase nanocrystal that the size effect of the dislocation redistribution essentially weakens. In the case of coherent boundaries, Γ_c always equals 1, while for slipping boundaries Γ_c depends on the geometry of crystallites and dislocations.

(3) For nanocrystals with the crystallite size less than the characteristic length Λ, a peculiar aging process occurs.

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