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Strengthening of nanocrystalline alloys by grain boundary segregations

A.G. Sheinerman✉

Institute for Problems of Mechanical Engineering RAS, 61, Bolshoi Pr. V.O., St. Petersburg, Russia, 199178

✉ asheinerman@gmail.com

Abstract. We suggest a model that describes the strengthening of nanocrystalline metallic alloys due to inhomogeneous grain boundary (GB) segregations. Within the model, inhomogeneous GB segregations are modeled by spherical dilatational inclusions whose elastic fields interact with lattice or GB dislocations. We consider two modes of plastic deformation of nanocrystalline alloys: GB sliding realized via the motion of GB dislocations over GBs and slip of lattice dislocations across grains. The calculations demonstrate that in the case of GB sliding, which occurs in nanocrystalline alloys with the finest grains, inhomogeneous segregations induce only moderate strengthening. In contrast, high strengthening due to GB segregations is achieved in nanocrystalline alloys with larger grain sizes, deformed through lattice dislocation slip. This implies that the preferred kind of segregations for maximum strengthening of nanocrystalline alloys can depend on their grain size.
Keywords: nanocrystalline alloys; grain boundaries; segregations; strengthening

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1. Introduction

Due to their ultrahigh strength and thermal stability, nanocrystalline metal alloys draw much attention last years [1-4]. In contrast to coarse-grained materials, where plastic deformation processes are carried out mainly due to the motion of dislocations within grains, in nanocrystalline alloys, the structure and composition of grain boundaries (GBs) have a primary effect on plastic deformation processes and strength. In particular, GB segregations of alloying elements have a great effect on the mechanical properties of nanocrystalline alloys. Although such segregations, under certain conditions, can lead to the embrittlement of nanocrystalline alloys, they can stabilize such alloys, inhibiting grain growth, and also lead to an increase in the ultimate strength or an increase in ductility. Examples of this are nanocrystalline steels [2], nanocrystalline silver-based alloys with ensembles of growth twins [3], and nanocrystalline Ni-Mo alloys [4] with record values of ultimate strength and hardness.

The strengthening effect of GB segregations has been attributed to various factors. For example, in [5,6] it was assumed that the increase in strength due to GB segregations is

associated with a decrease in the activation volume for the nucleation of dislocations, experimentally recorded [6] for the Zr-Nb alloy with GB segregations of sulfur. Computer simulations [7] of nanocrystalline Ag with Cu segregations demonstrated that strengthening can result from the inactivation of GB dislocation sources by GB segregations. At the same time, the results of computer simulations [8] show that strengthening can also stem from the hindering effect of GB segregations on dislocation motion across grains.

In [9], a moderate increase in the yield strength of nanocrystalline Al was demonstrated in the presence of Co segregations and the absence of a strengthening effect was documented for Mg segregations. An earlier work [10] showed the reverse (softening) effect of Pb segregations on the strength of nanocrystalline Al. In both cases, the simulation showed that the deformation of nanocrystalline Al (with Mg or Pb segregations) is carried out by GB sliding or GB sliding combined with GB migration. Therefore, it can be concluded that even if Pb segregations suppress intragranular dislocation slip, they can facilitate GB sliding, which leads to a decrease in yield strength.

At the same time, recent experiments with nanocrystalline Ni-Mo alloys [4] have shown that, in such alloys, low-temperature annealing, presumably leading to the appearance of Mo GB segregations [4], can, in contrast, suppress GB sliding and, thereby, significantly increase the hardness of such alloys. Computer simulations [11] of the deformation of Ag-Ni and Ag-Cu nanocrystalline alloys showed that the possibility of GB sliding in nanocrystalline alloys with segregations depends on the type of segregations. In particular, in this work, segregations in Ag-Cu alloys, distributed along the entire length of GBs, did not prevent GB sliding, which led to softening. In contrast, segregations in nanocrystalline Ag-Ni alloys, which formed clusters in certain areas of GBs, created obstacles for GB sliding, leading to high flow stresses in such alloys.

Thus, the results of experiments and computer simulations demonstrate that GB segregations can strengthen nanocrystalline alloys but the mechanism of strengthening is not clear enough yet. To fill this gap, here we suggest a model that describes the effect of clustered GB segregations on the yield strength of nanocrystalline metallic alloys deformed via GB sliding or through intragranular dislocation slip.

2. Strengthening of nanocrystalline alloys deformed via GB sliding

Consider a solid containing grain boundary (GB) segregations. Within the model, we treat the segregations as dilatational spherical inclusions of radius R_0 (Fig. 1a). We focus on the case of small GBs, whose size does not exceed several diameters of the inclusions and therefore assume that each GB contains not more than one inclusion. To examine the effect of the spherical inclusions on GB sliding, we assume that GB sliding occurs via the slip of edge GB dislocations over GBs. Each spherical inclusion creates an elastic stress field that creates forces acting on dislocations in its vicinity. Since the stress field of the inclusion is a short-range one and drops as R^{-3} outside the inclusion [12] (where R is the distance from the inclusion center), we assume that each inclusion at a GB can affect GB sliding only over this and adjacent GBs.

Now consider the geometry of an individual spherical inclusion at a GB (Fig. 1b). We introduce a Cartesian coordinate system (x, y, z) and a spherical coordinate system (R, θ, φ) with the origin at the center of the spherical inclusion (Fig. 1b). Here θ is the angle between the radius vector of a point and the z-axis, while φ is the angle between the projection of the radius vector onto the xy-plane and the x-axis. The y- and z-axes of the Cartesian coordinate system lie in the GB plane, while the x-axis is normal to the GB.

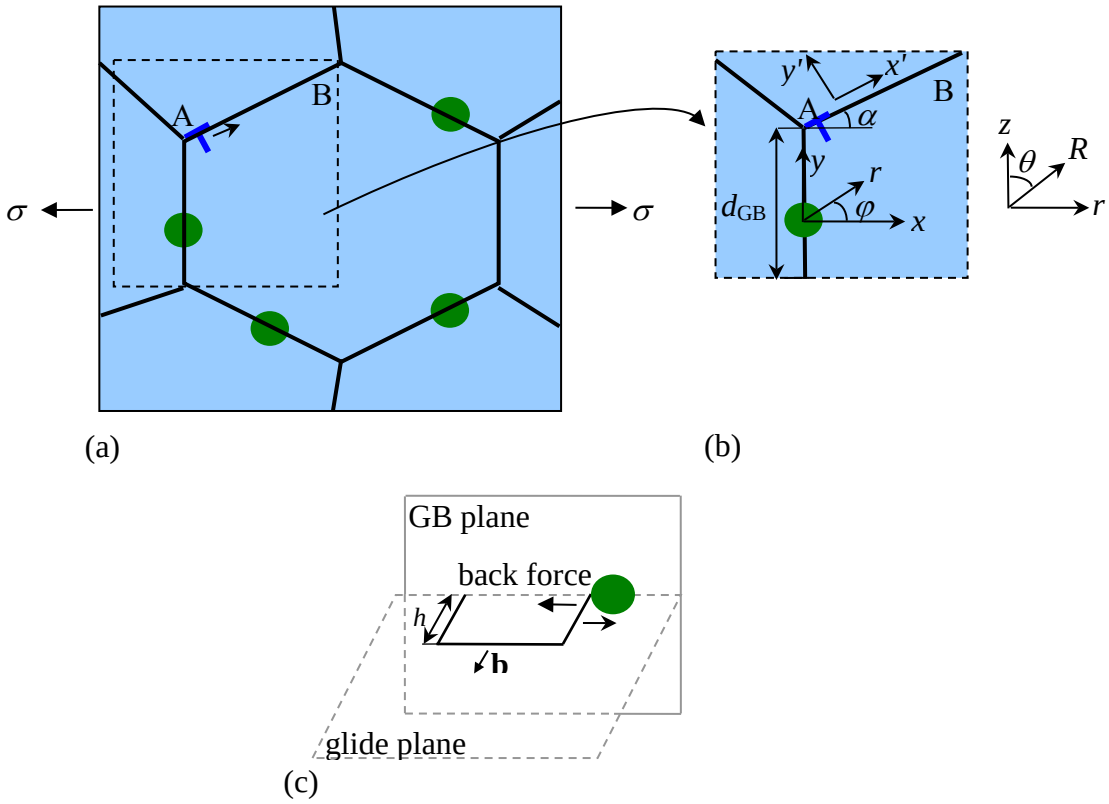

Fig. 1. Nanocrystalline solid with GB segregations. (a) A fragment of a nanocrystalline solid with GB segregations. GB sliding along GB AB occurs via the slip of a GB dislocation from triple junction A toward triple junction B. (b) Geometry of the coordinate systems used to calculate the stress field of a GB segregation. (c) Intragranular dislocation slip occurs via the generation of a glide dislocation loop at a GB and its expansion inside the grain interior. GB segregation exerts a back force on the segment of the expanding dislocation loop

In the examined case of the dilatational eigenstrain of inclusion, the eigenstrain tensor ε_{ij}^{*} can be written as

$$\varepsilon_{ij}^{*} = \varepsilon^{*}\delta_{ij}, \tag{1}$$

where $i, j = x, y, z$, ε^{*} is the lattice mismatch between the inclusion and the matrix, defined as (e.g., ([13])

$$\varepsilon^{*} = \frac{a_i - a_m}{a_m}, \tag{2}$$

a_i and a_m are the lattice parameters of the inclusion and matrix, respectively, and δ_{ij} is the Kronecker delta equal to unity if $i = j$ and to zero otherwise. In the linear approximation, we have:

$$a_s \approx a_m + 100(c_s - c_m)\Delta a, \tag{3}$$

where Δa is the change of the lattice parameter of the alloy associated with an increase of the solute concentration by 0.01 (that is, by 1 at.%), and c_s and c_m is the average solute concentration in the segregations and matrix, respectively.

In the approximation of an elastically homogeneous isotropic solid with the shear modulus *G* and Poison's ratio ν, the stress field of the inclusion can be written as [12]

$$\sigma_{RR} = 2A\begin{cases}1, R < R_0\\ (R_0 / R)^3, R > R_0\end{cases}, \quad (4)$$

$$\sigma_{\theta\theta} = \sigma_{\varphi\varphi} = A\begin{cases}-2, R < R_0\\ (R_0 / R)^3, R > R_0\end{cases}, \quad (5)$$

$$\sigma_{R\theta} = \sigma_{R\varphi} = \sigma_{\theta\varphi} = 0, \quad (6)$$

where $A = 2(1+\nu)G\varepsilon^* / [3(1-\nu)]$.

From formulae (4) to (6) it is easy to see that the stress σ_{xy} created by the spherical inclusion at the GB plane $x = 0$ is equal to zero. This implies that the inclusion does not create any forces on the dislocations moving over this GB. At the same time, it can affect the motion of dislocations over adjacent GBs. For definiteness, we calculate the effect of the inclusion stress field on the dislocation motion over GB AB (Fig. 1a,b). To do so, it is sufficient to calculate the maximum shear stress $\sigma_{x'y'}$ exerted by the inclusion at GB AB. (Here the x'- and y'-axes are directed as shown in Fig. 1b and make the angle α with the x- and y-axis, respectively.) Evidently, the maximum stress acts at triple junction A, which is closest to the inclusion.

In the cylindrical coordinate system (r, φ, z) with the origin in the inclusion center (Fig. 1b), the stress σ_{rr} can be written as

$$\sigma_{rr} = \sigma_{RR}\sin^2\theta + \sigma_{\theta\theta}\cos^2\theta. \quad (7)$$

In turn, at triple junction A characterized by $x = 0$, the stress $\sigma_{x'y'}$ follows as

$$\sigma_{x'y'} = (\sigma_{rr} - \sigma_{\varphi\varphi})\cos\alpha\sin\alpha = A\sin^2\theta\cos\alpha\sin\alpha\,(R_0 / R)^3. \quad (8)$$

For definiteness, we assume that triple junction A lies symmetrically with respect to the inclusion center, that is, occupies the region $-d_{GB}/2 < z < d_{GB}/2$, where d_{GB} is the GB length. Then, with an account for the relations $\sin^2\theta = r^2/(z^2 + r^2)$ and $R = (z^2 + r^2)^{1/2}$, the average stress $\bar{\sigma}_{x'y'}$ acting on the dislocation segment at triple junction A can be presented as

$$\bar{\sigma}_{x'y'} = (1/d_{GB})\int_{-d_{GB}/2}^{d_{GB}/2}\sigma_{x'y'}\,dz = \frac{2AR_0^3\sin(2\alpha)(6r^2 + d_{GB}^2)}{3r^2(4r^2 + d_{GB}^2)^{3/2}}. \quad (9)$$

Assuming that the distance from the inclusion center to the center of triple junction A is a random quantity in the interval $R_0 < r < d_{GB} - R_0$, the average value of $\bar{\sigma}_{x'y'}$ (averaged for various distances from the inclusion center to triple junction A) can be written as

$$<\bar{\sigma}_{x'y'}> = (1/d_{GB})\int_{R_0}^{d_{GB}-R_0}\bar{\sigma}_{x'y'}\,dr. \quad (10)$$

The stress $<\bar{\sigma}_{x'y'}>$ exerts a back force on the dislocation at triple junction A and thereby hinders GB dislocation slip over GB AB. To provide such slip, the applied load should increase (compared to the case where segregations are absent) in such a way as to increase the resolved shear stress in GB AB by $<\bar{\sigma}_{x'y'}>$. As a result, the contribution σ_{seg} of GB segregations to the yield strength can be estimated as $\sigma_{seg} = M <\bar{\sigma}_{x'y'}>$, where M is the Taylor factor approximately equal to 3.06 for metals and alloys with fcc crystal lattices [14].

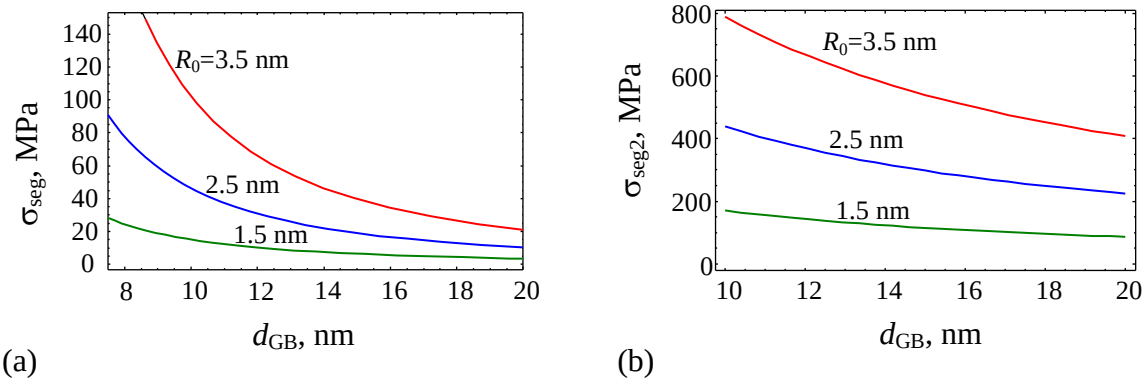

Fig. 2. Dependences of the stresses σ_{seg} (a) and σ_{seg2} (b) that characterize the GB segregation-induced strengthening in the 1570 Al alloy with GB Mg segregations in the case of plastic deformation via GB sliding and lattice dislocation slip, respectively, on the GB length d_{GB}

Now let us calculate σ_{seg} for the exemplary case of the 1570 Al alloy containing Mg segregations at GBs and characterized by the following parameter values [15]: $G = 27$ GPa, $\nu = 0.34$, $\varepsilon^* = 0.01$. We also put $\alpha = \pi/3$. The dependences of σ_{seg} on d_{GB} are shown in Fig. 2a, for various values of the segregation radius R_0. It is seen in Fig. 2a that σ_{seg} increases with an increase in the segregation radius and/or decrease in grain size. The grain size dependence of σ_{seg} is related to the reduction of the distance between segregations and the nearest triple junction with a decrease in grain size.

3. Strengthening of nanocrystalline alloys deformed via lattice dislocation slip

Figure 2a demonstrates that clustered GB segregations can increase the yield strength of nanocrystalline metallic alloys in the case where plastic deformation is realized via GB sliding. Now compare the effect of such segregations on GB sliding with their effect on intragranular dislocation slip. To do so, we adopt model [15], where the stress field of each GB segregation exerts a force on the straight segment of an expanding rectangular glide dislocation loop (Fig. 1c). Following [15], we assume that dislocation loops grow in the directions parallel to the GB planes without increasing their height (denoted as h in Fig. 1c). At the same time, in contrast to ref. [15], which considered ultrafine-grained alloys where each GB incorporates various segregations, here we focus on the case of nanocrystalline alloys, which contain no more than one segregation in each GB.

The hampering forces exerted by spherical segregations on the moving segments of the dislocation loops increase the yield strength. Using the calculation procedure suggested in ref. [15], we have calculated the contribution σ_{seg2} of GB segregations to the yield strength in the situation where plastic deformation is realized via the motion of lattice dislocations across grains from one GB to another. The dependences of σ_{seg2} on d_{GB} for the 1570 Al alloy containing Mg segregations at GBs are shown in Fig. 2b for $h = 3.7$ nm and the values of other parameters specified above. It is seen in Fig. 2b that the stress σ_{seg2} increases with a decrease in grain size and/or increase in the segregation radius, similarly to the behavior of the stress σ_{seg}. Also, the comparison of Figs. 2a and 2b clearly demonstrates that for the same grain size and segregation radius, σ_{seg2} is much larger than σ_{seg}. This implies that clustered segregations are more effective in hampering intragranular lattice slip than in preventing

GB sliding. Thus, it is logical to assume that clustered segregations are not very effective for strengthening nanocrystalline metallic alloys with finest grains, where the presence of the inverse Hall-Petch dependence associated with GB sliding leads to softening. At the same time, clustered segregations should be very effective for strengthening nanocrystalline metallic alloys with larger grain sizes, which deform through lattice dislocation slip across grains.

4. Conclusions

In summary, GB segregations can exert a high strengthening effect in nanocrystalline metallic alloys. For clustered GB segregations, the highest strengthening is achieved in the case of not very small grains, when nanocrystalline alloys deform via lattice dislocation slip. For nanocrystalline alloys with the finest grains, clustered segregations can provide only moderate strengthening. Therefore, one can assume that the ultrahigh strengthening of nanocrystalline alloys, deformed via GB sliding, due to GB segregations [4] is associated with the choice of the alloying elements that promote GB sliding and their homogeneous segregations along entire GBs. Thus, one can assume that the most effective kind of GB segregations in nanocrystalline alloys can depend on their grain size. For nanocrystalline alloys with the finest grains, the highest strengthening can be achieved in the case of homogeneous GB segregations, while for nanocrystalline alloys with higher grain sizes inhomogeneous clustered segregations can provide the highest strengthening.

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THE AUTHOR

Sheinerman A.G.
e-mail: asheinerman@gmail.com
ORCID: 0000-0001-9909-2950