Mechanical Grain Growth in Nanocrystalline Copper

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Nanograined materials have some unusual properties. To maintain the small size of the grains, grain growth should be avoided. But recently grain growth has been observed under an indenter at liquid-nitrogen temperatures. Such grain growth has never been reported before. How can this happen and how can it be prevented? These questions are answered here using a simple tilt boundary. It is found that high purity and nonequilibrium structure are necessary conditions for mechanical grain growth. The material must be pure enough so that free dislocations are available to move out of the boundary. But the boundary should not be in the lowest-energy state so that extra dislocations are available to be emitted by stress. Based on these conditions, methods can be devised to avoid low temperature grain growth.

Introduction.—Mechanical grain growth was observed recently by Zhang *et al.* [1,2] in nanocrystalline Cu under an indenter at liquid-nitrogen temperatures ($-190\,°C$). Since the temperature was so low, thermally activated processes must be inoperative. Hence the grains must have grown by mechanical means alone. This unusual phenomenon has never been reported before. What is the cause and under what conditions does it occur? Other observers have also reported grain growth during deformation of nanocrystalline materials [3–6]. However, since these experiments were done at room temperature or under electron irradiation, the possibility of grain boundary diffusion could not be ruled out. Atomistic simulation of Haslam *et al.* [7] also indicated stress enhanced grain growth and Winning [8–10] showed a bicrystal tilt or twist boundary can be moved by stress alone at high temperatures (500 K and up) for Al. But again, all of these require thermal activation for grain boundary motion. Nobody has ever observed grain growth in Cu at liquid-nitrogen temperatures before Zhang *et al.* [1,2].

The results of Zhang *et al.* [1,2] are described briefly as follows: the indentation hardness decreased with time for IGC (inert gas condensation using 99.999% pure, 98%–99% dense) copper, faster at $-190\,°C$ than at room temperature and faster for small grains (11 nm) than large grains (200 nm). For coarse grain copper (same purity, submicron grain size, annealed) the hardness did not change much with time in the same temperature range. Grains grew under the indenter, faster at $-190\,°C$ than at room temperature. After 30 minutes, grains grew from 20 nm to 200 nm at room temperature, but from 20 nm to 400 nm at $-190\,°C$.

In this communication, an attempt will be made to understand why nanograins grow under indentation while micrograins do not and why nanograins grow faster at low temperatures than at room temperature. Such understanding will undoubtedly enable methods to be developed to prevent such growth.

Nanograin boundaries are purer.—As observed by Terwilliger and Chiang [11], segregation of Ca to grain boundaries of TiO_2 became less when the grain size decreased below 150–350 nm due to an increase of grain boundary area. The thermodynamic equilibrium between the impurities and grain boundaries for nanocrystalline materials has been analyzed by Weissmuller [12] extending an earlier treatment by McLean [13], Cahn [14], and others. Here it is shown how a critical grain size can appear. Let N_β be the total concentration of an impurity β per unit volume; some of that, $N_{\beta m}$ is dissolved per unit volume of the grains and the rest, $N_{\beta b}$, is segregated per unit area of the boundaries. Materials balance gives

$$N_{\beta m}V + N_{\beta b}A = N_\beta V, \tag{1}$$

where V is the volume of the grains and A is the area of the boundaries. If A/V is taken as $3/d$ [12] with d being the grain size, Eq. (1) becomes

$$N_{\beta m} + \frac{3N_{\beta b}}{d} = N_\beta. \tag{2}$$

Now let $N_{\beta b}^0$ be the saturation amount of impurity β per unit area of grain boundaries and $x = N_{\beta b}/N_{\beta b}^0$ be the extent of saturation or the fraction of possible sites occupied by the impurity, a quantity between 0 and 1. The equilibrium between the impurity in the matrix and that in the grain boundaries requires:

$$\frac{x}{1-x} = KN_{\beta m} = K\left(N_\beta - \frac{3xN_{\beta b}^0}{d}\right), \tag{3}$$

where K is an equilibrium constant. Equation (3) gives the grain size:

$$\frac{d}{3KN_{\beta b}^0} = \frac{x}{KN_\beta - \frac{x}{1-x}}. \tag{4}$$

Since the grain size must be positive, there is a maximum x which depends only on KN_β:

$$x_m = \frac{KN_\beta}{1 + KN_\beta}. \tag{5}$$

Substituting this into Eq. (4) gives

$$\frac{d}{3KN^0_{\beta b}} = \frac{x(1 - x_m)(1 - x)}{x_m - x}. \tag{6}$$

A plot of d (in units of $3KN^0_{\beta b}$) versus x is shown in Fig. 1 in which x_m is taken as 0.98. A sudden transition can be seen at some grain size. If a critical grain size d_c is defined at $x = 0.5$:

$$\frac{d_c}{3KN^0_{\beta b}} = \frac{0.5}{KN_{\beta} - 1} = \frac{0.5(1 - x_m)}{2x_m - 1}. \tag{7}$$

It is seen that the critical grain size increases with decreasing total impurity content. Within an order of magnitude change in grain size around the critical grain size, the equilibrium segregation can change from $x = 0.9$ to 0.1.

Hence for any nominal impurity level, nanograin boundaries could be much purer if the grain size is below the critical size. Thus if the Hall-Petch slope relates to the impurity level in the grain boundaries, it is expected that the slope will decrease with decreasing grain size in the critical grain size regime. This is evidenced by a recent collection of literature data by Takeuchi [15]. Any model attempting to understand the grain size effect of strength without taking into consideration the grain size effect of impurity levels in the grain boundaries must be incomplete. If the properties of a grain boundary change with grain size, this change should be included in any model.

Removal of dislocations from a pure grain boundary.— Now let us see the effect of impurities on the ease of removal of dislocations from a grain boundary. For a simple tilt boundary in which the spacing between dislocations is h, the shear stress to remove a free dislocation is given by Li [16]:

$$\sigma_{xy} = \frac{-\mu b}{2\pi h(1 - \nu)}\left[\frac{2\pi^2(x/h)}{\cosh(2\pi x/h) - 1} - \frac{h}{x}\right], \tag{8}$$

where μ is the shear modulus and ν is the Poisson ratio of the material, the wall is in the yz plane, and the dislocations are parallel to the z axis. The free dislocation is now at $(x, 0)$ while still parallel to the z axis. The external shear stress σ_{xy} is needed to hold the free dislocation at $(x, 0)$.
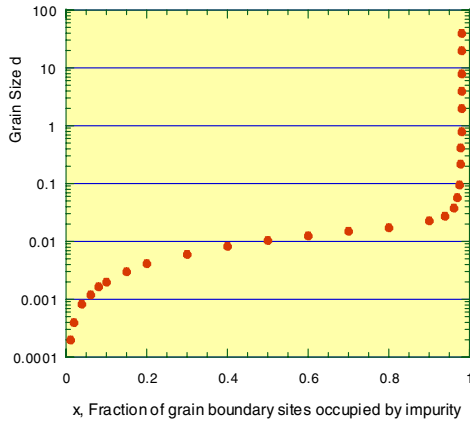

FIG. 1 (color online). The effect of grain size on the impurity segregation at the grain boundaries.

The variation of this shear stress with x is shown in Fig. 2 and it is seen that the external stress needed to remove the free dislocation is about $1.1\mu b/2\pi h(1 - \nu)$. This is not a small stress, especially if h is small. For example, if $b = h$, this stress is about 10 GPa, higher than the yield stress of the nanocrystalline Cu. So if there is only one free dislocation in the wall, it will be difficult to remove. It is to be noted that Eq. (8) is for an equilibrium boundary, namely, a boundary of the lowest-energy possible consistent with the angle of misfit. The size of the grain or the boundary has no effect as long as the stress field corresponds to that of an infinite wall, namely, the lowest-energy state. See later for a possible nonequilibrium boundary.

However, the stress is reduced when there are two free dislocations in the wall as shown also in Fig. 2. Instead of Eq. (8), the stress required to move the two free dislocations together to the position x is now

$$\sigma_{xy} = \frac{-\mu b}{2\pi h(1 - \nu)}\left[\frac{2\pi^2(x/h)}{\cosh(2\pi x/h) - 1} - \frac{h}{x} - \frac{xh(x^2 - h^2)}{(x^2 + h^2)^2}\right]. \tag{9}$$

The external shear stress needed is now $0.935\mu b/2\pi h(1 - \nu)$ to remove both dislocations. Since high purity of a grain boundary means more free dislocations in the grain boundary, it is seen that increasing purity makes a lot of difference for the stress needed to remove dislocations.

For 3 free dislocations, the situation is a little more complicated. Two variables, x_0 and x, are needed to describe the structure. The external stress needed to maintain equilibrium is given by the following two simultaneous equations:

$$\sigma_{xy}\frac{2\pi h(1 - \nu)}{\mu b} + A\left(\frac{x_0}{h}\right) - \frac{h}{x_0}$$
$$- 2B_1\left(\frac{x_0}{h}\right) + 2C_1\left(\frac{x_0}{h}, \frac{x}{h}\right) = 0,$$
$$\sigma_{xy}\frac{2\pi h(1 - \nu)}{\mu b} + A\left(\frac{x}{h}\right) - \frac{h}{x}$$
$$- B_1\left(\frac{x}{h}\right) - B_2\left(\frac{x}{h}\right) + C_1\left(\frac{x}{h}, \frac{x_0}{h}\right) = 0, \tag{10}$$
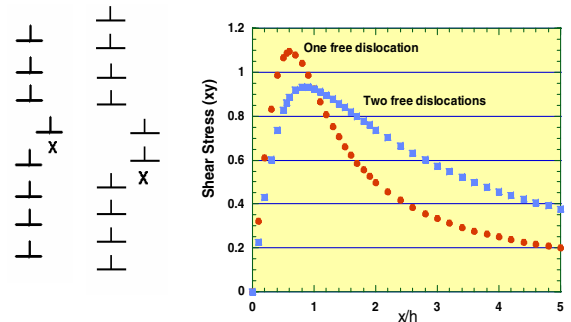

FIG. 2 (color online). Stress required to remove one or two free dislocations from wall showing it is easier to remove 2 than 1 [unit of stress: $\mu b/2\pi h(1 - \nu)$].

where

$$A(p) \equiv \frac{2\pi^2 p}{\cosh(2\pi p) - 1} \tag{11}$$

$$B_1(p) \equiv \frac{p(p^2 - 1)}{(p^2 + 1)^2} \qquad B_2(p) \equiv \frac{p(p^2 - 4)}{(p^2 + 4)^2} \tag{12}$$

$$C_1(p, q) \equiv (p - q)\frac{(p - q)^2 - 1}{[(p - q)^2 + 1]^2}. \tag{13}$$

As shown in Fig. 3, there are four different paths to remove the 3 free dislocations with one of the paths the lowest stress required which is about $0.82\mu b/2\pi h(1 - \nu)$, lower again than that to remove 2 free dislocations. Starting from $x_0 = 0$ there are actually only 2 paths as shown in Fig. 4. One is a special path of $x_0 = x$, namely, the 3 dislocations moving together as a short wall. This may not be the lowest stress needed but it is close. On the other hand, this is probably the path starting from the original wall. So $x_0 = x$ may be an actual path for which the stress required is $0.87\mu b/2\pi h(1 - \nu)$ which is still less than that for 2 free dislocations.

However, the stress required to remove more than 3 dislocations is about $0.8\mu b/2\pi h(1 - \nu)$ independent of the number of free dislocations. This is also the stress to move the whole boundary for very pure materials so that all the dislocations are free. Details of these calculations will be submitted elsewhere. However, the distance the free dislocations have to travel before the maximum stress is reached is about $0.5Nh$, where N is the number of free dislocations. So if the grain size is small, the free dislocations may reach the other grain boundary before the maximum stress. In other words, the free dislocations in one grain boundary may be removed to reach the other boundary at a stress less than $0.8\mu b/2\pi h(1 - \nu)$.

Removal of extra dislocations from a pure grain boundary.—The foregoing analysis seems to suggest that purity is necessary but not sufficient for dislocations to be removed by external stress from a grain boundary, since the stress needed is still high even if the grain boundary is very pure so that many dislocations are not pinned at all. But the nanograined material is made by energetic processes such as inert gas condensation; the resulting grain bounda-

ries may not be in the lowest-energy form. Löffler and Weissenmüller [17], based on x-ray atomic distribution functions of nanocrystalline Pd within 10 days of preparation by inert gas condensation, found 10% of atoms were located on nonlattice sites with little or no atomic short range order. This corresponds to about two monolayers of atoms on nonlattice sites at the grain boundaries as compared to one quarter of a monolayer in aged or annealed samples. Kumar *et al.* [18] made a recent review of the literature and, while showed some evidence of equilibrium boundaries in the TEM, did allow nonequilibrium structure in as-deposited and as-deformed materials. Armstrong *et al.* [19] also mentioned the possibility of unusual disorder in grain boundaries as suggested by molecular dynamics simulation of Van Swygenhoven *et al.* [20]. Hence the grain boundaries in as-deposited conditions may not have the lowest-energy configuration. Here we examine one type of nonequilibrium structure, namely, the existence of extra dislocations in as-deposited nanocrystalline copper especially at low temperatures. Extra dislocations have already been suggested to exist in grain boundaries by Zhu *et al.* [21].

Figure 5 shows the situation of one extra dislocation existing along the same slip plane as a free dislocation in the wall. The stress to maintain equilibrium is given by the following pair of simultaneous equations:

$$\sigma_{xy}\frac{2\pi h(1 - \nu)}{\mu b} + A\left(\frac{x_0}{h}\right) - \frac{h}{x_0} + \frac{h}{x_0 - x} = 0,$$
$$\sigma_{xy}\frac{2\pi h(1 - \nu)}{\mu b} + A\left(\frac{x}{h}\right) - \frac{h}{x} + \frac{h}{x - x_0} = 0. \tag{14}$$

The zero stress equilibrium position with one dislocation at $+0.475h$ and the other one at $-0.475h$ is actually a stable position. Such structure was observed in real crystals [22,23]. Since it is a stable structure, external stress is needed to remove the extra dislocation from the wall. The required stress is about $0.12\mu b/2\pi h(1 - \nu)$ which is only about 10% of what is needed to remove a single free dislocation from the wall.

To see whether the stress required is less with more extra dislocations in the wall, Fig. 6 shows the situation for 2 extra dislocations. At zero stress, the equilibrium positions are for one set at $+0.636h$ and the other set at $-0.636h$.
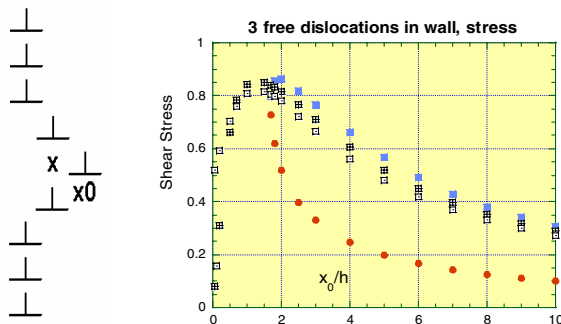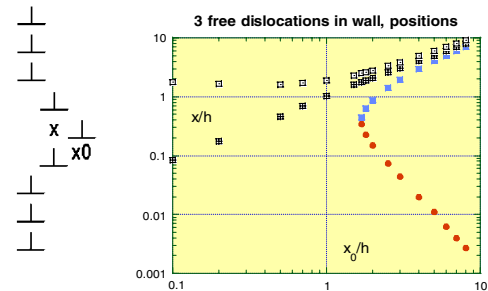
FIG. 3 (color online). Stress required to remove 3 free dislocations from wall, showing 4 different paths. [Unit of stress: $\mu b/2\pi h(1 - \nu)$.]

FIG. 4 (color online). The four different paths of removing 3 free dislocations in wall, showing one special path of $x_0 = x$.
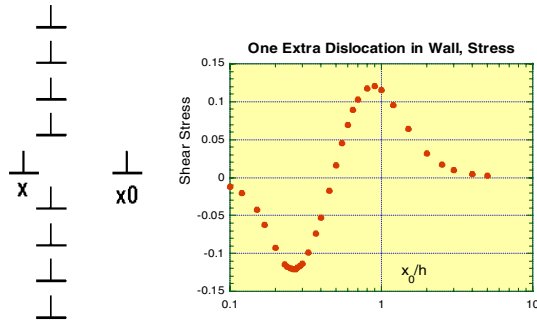
One Extra Dislocation in Wall, Stress

FIG. 5 (color online).   Stress required to remove an extra dislocation in wall, showing a much lower stress than to remove a free dislocation [unit of stress: $\mu b/2\pi h(1-\nu)$].

This is also a stable structure and requires external stress to decompose it. It is seen that the stress required is now $0.077\mu b/2\pi h(1-\nu)$, which is smaller than that for one extra dislocation.

It turns out that the stress needed to remove more extra dislocations is about $0.06\mu b/2\pi h(1-\nu)$, not much smaller than the 2 extra dislocations. Details of these calculations will be submitted elsewhere. However, the distance traveled by the finite wall before it can be removed is now pretty far away from the grain boundary. So when the grain size is small, the extra dislocations can be removed by reaching the other boundary at a lower stress. This is another reason why mechanical grain growth can take place in nanocrystals but not in microcrystals. These calculations will be reported later.

Extra dislocations or ledges in the grain boundary were suggested [24] as a source of yielding which provided a way of understanding the Hall-Petch relation without pile-ups. Now it is suggested that extra dislocations in the nanocrystalline grain boundary can initiate mechanical grain growth even at liquid-nitrogen temperatures.

Conclusions.—The foregoing analysis clarifies the unusual phenomenon of mechanical grain growth at liquid-nitrogen temperatures reported recently for the first time [1,2]. Grain boundaries can be decomposed under stress by first removing the extra dislocations. Once the extra dislocations are removed, the angle of misfit of the boundary
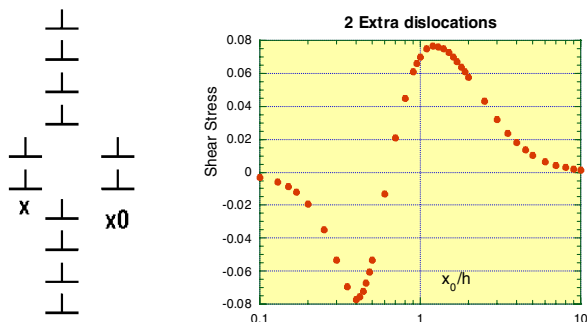

2 Extra dislocations

FIG. 6 (color online).   Stress required to remove 2 extra dislocations from wall, showing that the stress is less than that required to remove only one. [Unit of stress: $\mu b/2\pi h(1-\nu)$.]

decreases so the whole boundary can move under stress or disintegrates by emitting all the free dislocations. The emitted dislocations then approach nearby boundaries to remove their extra dislocations. Repeated operation of these processes causes the grains to grow simply under the action of stress without any diffusional processes involved. However, two necessary conditions must be met: high purity boundaries (below critical grain size with many free dislocations in the boundary) and nonequilibrium structures (with many extra dislocations in the boundary). This explains why mechanical grain growth is faster at liquid-nitrogen temperatures which tend to maintain the high energy structure.

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