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A New Model for Inverse Hall-Petch Relation of Nanocrystalline Materials

Ali Shafiei Mohammadabadi and Kamran Dehghani

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In the present article, a new model for inverse Hall-Petch relation in nanocrystalline materials has been proposed. It is assumed that lattice distortion along grain boundaries can cause internal stresses and high internal stresses along grain boundaries can promote the grain boundary yielding. The designed model was then verified using the nanocrystalline-copper data. The minimum grain size for inverse Hall-Petch relation is determined to be about 11 nm for Cu.

Keywords Hall-Petch equation, internal stress, nanocrystalline materials, yield strength

1. Introduction

The strength of polycrystalline materials is expected to increase with decreasing grain size. For coarse-grain materials, the size effect on flow stress is well known and is given by the empirical Hall-Petch relationship, which suggests that the yield stress increases with decreasing grain size (Eq 1).

$$\sigma = \sigma_0 + \frac{K}{\sqrt{d}} \quad \text{(Eq 1)}$$

where σ is the yield stress, σ_0 the friction stress, K the Hall-Petch slope, and d is the grain size. However, the relationship between the yield strength of the nanostructure materials and the grain size is very complicated. Furthermore, when the grain size of nanostructure materials is smaller than a critical value, the inverse Hall-Petch relation is observed (Ref 1-3).

As the inverse Hall-Petch phenomenon has not yet been clearly identified, numerous studies are carried out to make it more clear (Ref 4, 5). General conclusions of cited articles are based on this fact that as the size of the crystalline grain reduces, the influence of grain boundaries can be very important. That is because as the size of the crystalline grain reduces into the nanometer range the volume fraction of the grain boundaries and triple junctions increases very rapidly (Ref 6, 7) and consequently the activity of grain boundaries increases (Ref 8, 9). Thus, it seems that for an accurate investigation, two above roles of grain boundaries should be considered simultaneously. In the present article, a new approach for considering the effects of grain boundary was made. The presented model takes into account simultaneously the effects of both the volume fraction of grain boundaries and the activity of grain boundaries. Besides, it is assumed that lattice distortion along grain boundaries can cause internal stresses. High internal stresses along grain boundaries can promote the deformation in the grain-boundary layers when grain boundary yielding can be considered as general yielding.

Ali Shafiei Mohammadabadi, Department of Material Science and Engineering, Sharif University of Technology, Tehran, Iran; and **Kamran Dehghani**, Department of Mining and Metallurgical Engineering, AmirKabir University of Technology, Tehran, Iran. Contact e-mail: Alishland@yahoo.com.

2. The Developed Model

In general, in nanocrystalline materials, grain boundaries are normally in a metastable or non-equilibrium state. That is in contrast to grain-boundaries status in coarse-grained materials (Ref 10). Furthermore, high-resolution transmission electron microscopy studies have shown that the local atomic structure of grain boundaries in nanostructure materials is similar to that in coarse-grained metals, except that high internal stresses and lattice distortions exist near the boundaries in the former (Ref 11-13). Bachurin et al reported high shear stresses along grain boundaries and proposed that these stresses tend to displace the grain boundaries (Ref 10). Kozlov et al measured the internal stresses along grain boundaries of UFG copper having the average grain size of 210-120 nm (Ref 14). Cited author also found that internal stresses increase up to a value of 80 ± 90 MPa near grain boundaries. Therefore, we can suppose that when a structure experiences external loads, grain boundary tolerates external stresses plus high internal stresses along grain boundaries. Therefore, the equation for the stress along grain boundary can be:

$$\sigma_{gb} = \frac{\sigma - \sigma_g f_g}{f_{gb}} + \sigma_{in} \quad \text{(Eq 2)}$$

where σ_{gb} is the grain boundary stress, σ is external stress, σ_{in} is internal stress along grain boundary that depends on parameters such as grain boundary thickness, lattice distortions near grain boundaries and grain size, f_{gb} the volume fraction of grain boundary, and f_g is the volume fraction of crystalline part. The first term of Eq 2 drives from the composite model that *is* used in many works (Ref 6, 15-17). In the present article, it is assumed that high grain boundary stress (σ_{gb}) can promote more deformation in grain boundaries and general yield can occur in these areas by grain boundary deformation

instead of interior grain deformation. Many atomistic simulations and physical experiments proved this theory (Ref 11, 18-23). The past work demonstrated that as the grain size decreases, intragranular plasticity driven by dislocation mechanisms becomes more difficult at nanometer-scale grain sizes, and that the macroscopically imposed deformation is accommodated by grain-boundary sliding and separation (Ref 24).

A stress-type threshold behavior for grain boundary deformation was considered in the past works (Ref 7, 16). They considered a constant amount for the yield strength of the grain boundary (e.g. k'). Therefore, the general relation for yielding can be written as:

$$(\sigma_{gb}) = k' \quad \text{(Eq 3)}$$

Solving Eq 2 and 3 yields:

$$k' = \frac{\sigma - \sigma_g f_g}{f_{gb}} + \sigma_{in} \quad \text{(Eq 4)}$$

or

$$\sigma = k' f_{gb} + \sigma_g f_g - \sigma_{in} f_{gb} \quad \text{(Eq 5)}$$

By substituting $f_g = (1 - f_{gb})$ in Eq 5, external stress (σ) for yielding is obtained as following:

$$\sigma = \sigma_g + (k' - \sigma_g) f_{gb} - \sigma_{in} f_{gb} \quad \text{(Eq 6)}$$

In case of coarse-grain materials, the third item is very small and can be ignored. So, the first two terms of Eq 6 is compared with Hall-Petch equation (Eq 1) ($\sigma_g = \sigma_0$, $(k' - \sigma_g) \cdot f_{gb} = K/\sqrt{d}$) (Ref 7). Therefore, Eq 3 can be rewritten as below:

$$\sigma = \sigma_0 + \frac{K}{\sqrt{d}} - \sigma_{in} f_{gb} \quad \text{(Eq 7)}$$

This formula shows that when grains are nanosize and f_{gb} is noticeable, it is not only the size of crystalline grain, but also the grain boundary condition that contributes to the stress of yield.

3. Results and Discussion

Fan et al. (Ref 25) verified their experimental data according to Hall-Petch relation and found $\sigma_0 = 96.7$ MPa and $K = 3273$ MPa nm$^{1/2}$ for copper. Furthermore, the cited authors suggested the following equation for f_{gb}:

$$f_{gb} = 1 - \left(1 - \frac{w}{d}\right)^3 \quad \text{(Eq 8)}$$

where w is the width of grain boundary, which it is approximately about 0.5-1 nm. This finding is in accordance with the results reported in Ref 6. Substituting σ_0, K, and Eq 8 into Eq 7 gives the following relation for σ:

$$\sigma = 96.7 + \frac{3273}{\sqrt{d}} - \sigma_{in}\left(1 - \left(1 - \frac{w}{d}\right)^3\right) \quad \text{(Eq 9)}$$

where the amount of σ_{in} can be determined from Eq 10 (Appendix 1):

$$\sigma_{in} = G_g \cdot \gamma_g = \frac{2G_g \cdot \delta}{d} \quad (\sigma_{in} < \sigma_{id}) \quad \text{(Eq 10)}$$

where γ_g is the shear strain within the grains but adjacent to grain boundaries, δ represents the distance of mismatch or distortion in grains but in the vicinity of grain boundaries that is equal to half of the interplanar distance or half of grain boundary thickness for Cu (Ref 26). G_g is shear modules of grain next to grain boundaries and σ_{id} shows the maximum coherency strength along grain boundaries and is assumed to be about 2700 MPa for Cu.

By substituting Eq 10 into Eq 9, the amount of σ can be obtained, as shown in Fig. 1. The comparison between the results based on Hall-Petch equation and the predicted ones by the new model is also shown in Fig. 1. This figure illustrates that the stress along grain boundaries strictly can affect the yield strength of nanostructure materials especially in grain size below 50 nm. From Fig. 1 the critical size of crystalline grains of nanometer Cu is determined to be about 11 nm which is relatively comparable with 18 nm obtained by Fedorov et al. (Ref 4) and 14 nm by Masumura et al. (Ref 5), but smaller than 50 nm found by Arzt (Ref 27). As mentioned, in case of 1-20 nm, the grain boundary yielding can be dominating as the general yielding leading to the drop in yield stress at 11 nm. In other words, dislocation activity below a critical grain size is ceased and other mechanisms can become the main deformation mechanism leading to softening and lowering the yield strength. The results of current model, presented in Fig. 1, suggest that, in case of 1-20 nm, thick layer of grain boundary structure is likely much weaker than the crystalline material leading to a drop in yield stress at 11 nm. In other words, the extensive internal stress built up in grain boundary regions can cause grain boundary yielding to release the stress so as to reduce the stored energy. Deformation mechanisms that lead to grain boundary yielding may include sliding or the grain rotation following grain boundary shear. As a result, it should be mentioned that the internal stress along grain boundaries can be significantly released/decreased at grain sizes less than 11 nm leading to Hall-Petch inverse effect, e.g. here for copper at this grain size.

Furthermore, referring to Fig. 1, one can conclude that if the amount of internal stresses is decreased then the decrease in yield strength can be postponed. This can be a great success in field of nanostructure materials. Considering Eq 10, it is obvious that if one can reduce the grain boundary distortion

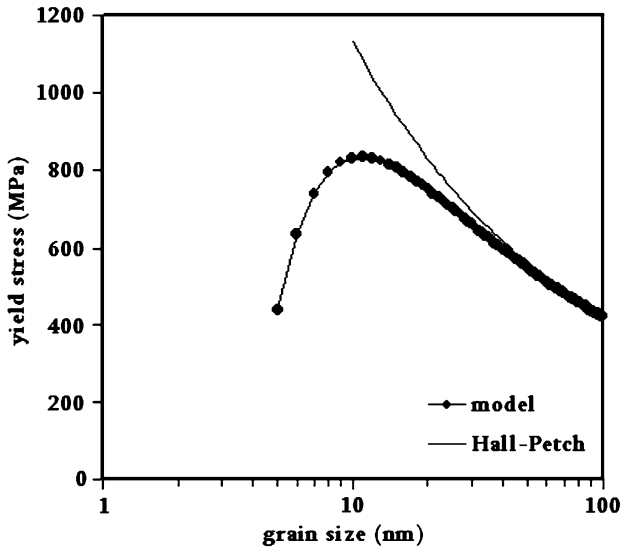

Fig. 1 Predicted yield stress as a function of grain size in Cu

(and so reducing the γ_g), the internal stresses can be decreased and consequently the yield strength is increased. The past works proved this theory (Ref 12, 28). Sergueeva et al. investigated the mechanical properties of pure Ti at room temperature (Ref 12). They found that after short annealing at low temperatures (250-300 °C), an increase in yield strength and ductility was observed (Fig. 2). It was pointed out by Sergueeva et al. that selected area diffraction patterns (SADP) obtained from as-processed Ti confirms the existence of high angle grain boundaries and high internal stresses. However, after short annealing at low temperatures SADP confirms the significant decrease in lattice distortion without visible grain growth. Therefore, one may conclude that the increase in strength after annealing may be related to significant decrease in lattice distortion adjunct to grain boundaries without any change in grain state or grain growth. In other words, such grain boundaries switch from non-equilibrium state to equilibrium condition during annealing at low temperature. Therefore, the initial increase in hardness/strength may be attributed to changing in grain boundaries state rather than the grain state.

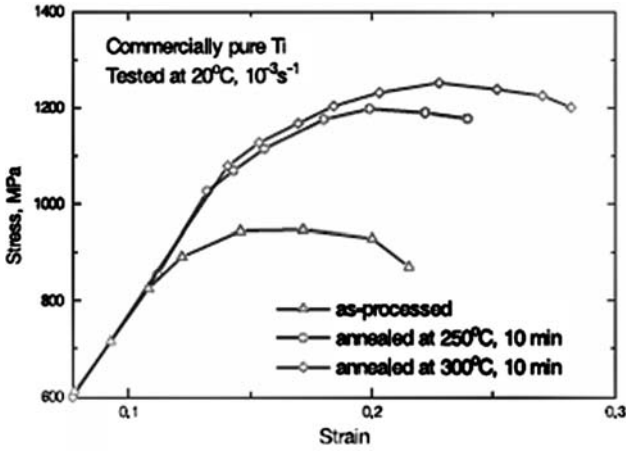

Fig. 2 Stress-strain curves for Ti in as-prepared and annealed state at room temperature (Ref 12)

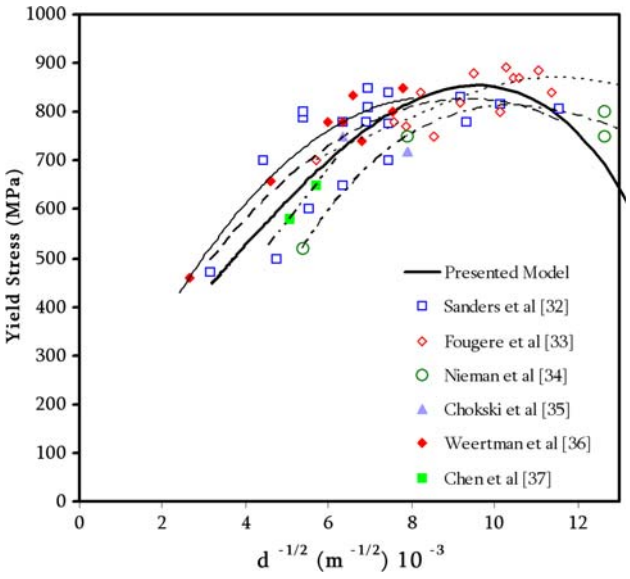

Fig. 3 Comparison of experimental data and predictions of model

Moreover, Namilae et al. investigated the relation between grain boundary energy and grain boundary sliding (Ref 28). The cited authors found that a higher energy grain boundary has more disordered structure. Hence, there is a higher stress concentration (so high σ_{in}) and consequently higher tendency to slide than low energy boundaries. In another words, cited authors showed that high internal stress along grain boundaries can promote grain boundary deformation and this fact confirms the results reported here.

The comparison of the yield strength by model and the experimental results is plotted in Fig. 3. As it is observed, there is a good agreement between the experimental results and predicted amounts. The same trend was also reported by other researchers (Ref 29-31).

4. Conclusion

A theoretical model is proposed in this paper to explain the grain-size dependence of the flow strength of nanostructure materials. The presented model shows that internal stress along grain boundaries can strongly change the yield strength of nanostructure materials. Furthermore, the model predicts that decreasing the internal stresses along grain boundaries can cause a delay in strength softening. The critical size of crystalline grains of nanometer Cu is determined to be 11 nm.

Appendix 1

To calculate the amount of σ_{in} we need an estimate of shear strain along grain boundaries (γ_g) or shear lattice distortion occurring within the grains. For quantitative analysis, consider Fig. A.1. It depicts that the shear strain along grain boundaries can be calculated as below (Eq A.1)

$$\gamma_g = \frac{2\delta}{d} \qquad \text{(Eq A.1)}$$

where δ represent the distance of mismatch in grains near grain boundaries and d the width of grain. Using the molecular dynamic simulation, Zhou et al. (Ref 26) gained the

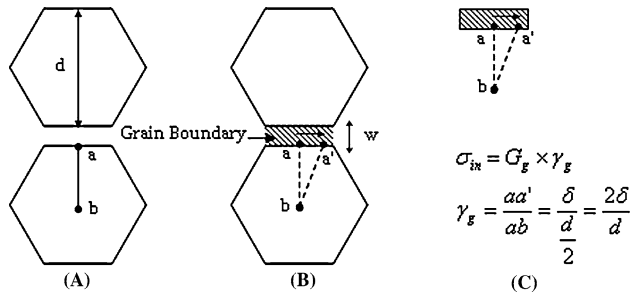

Fig. A.1 A simple model for estimation of internal stress along grain boundary. (1) Two separated grains. (2) Two joined grains; existence of grain boundary and $|aa'|$ shear distortion because of grains coincidence along grain boundary. (3) Estimation of σ_{in} that is caused by γ_g

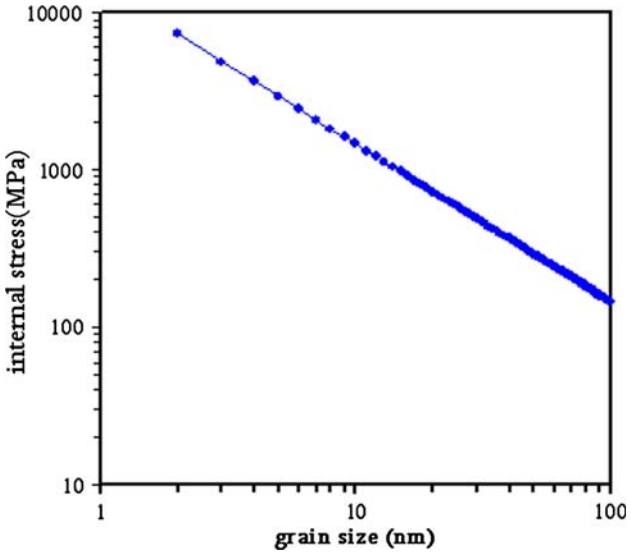

Fig. A.2 Internal stress as a function of grain size

similar equation (Ref 26). Furthermore, cited authors found that δ is about half of the inter-plane distance for Cu, 1/8 of the inter-plane distance for Al. Therefore, this shear distortion is negligible for grains of conventional size, but significant for nanosized grains (Ref 26). Therefore, the amount of internal stresses along grain boundaries can be determined from the following equation:

$$\sigma_{in} = G_g \cdot \gamma_g = \frac{2G_g \cdot \delta}{d} \qquad \text{(Eq A.2)}$$

where the G_g is shear modules of grain near grain boundaries. The local elastic constants, for the grain boundary region, have been calculated to be about 60-75% of the crystalline values (Ref 7, 15). Equation A.2 shows that high lattice distortion or small grain size can cause high internal stress along grain boundaries.

Figure A.2 shows that the σ_{in} is a function of grain size. For the calculation presented in Fig. A.2, the following values are used for parameters in Eq A.2: $\delta = \frac{w}{2} = 0.25\,\text{nm}$, $G_g = 30\,\text{GPa}$.

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