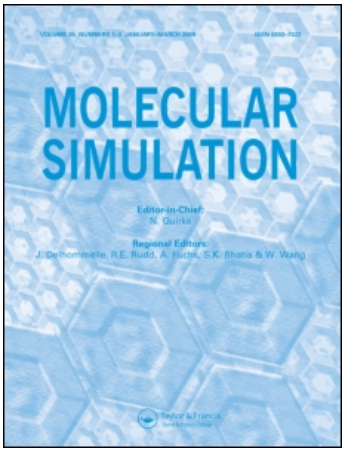

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Rajgarhia, R. K. , Koh, S. W. , Spearot, D. and Saxena, A.(2008) 'Microstructure stability of nanocrystalline materials using dopants', Molecular Simulation, 34: 1, 35 — 40
To link to this Article: DOI: 10.1080/08927020701730427
URL: http://dx.doi.org/10.1080/08927020701730427

Molecular Simulation
Vol. 34, No. 1, January 2008, 35–40

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Microstructure stability of nanocrystalline materials using dopants

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(Received 13 August 2007; final version received 6 October 2007)

By definition, nanocrystalline materials have grain sizes, d, less than 100 nm. Due to their reduced grain size, nanocrystalline materials have superior mechanical properties compared to their microcrystalline counterparts. Loss of these unique properties due to grain growth under the effect of high temperature and stress is a limitation to their use in many applications. Recently it has been proposed to use dopants (alloying elements) to reduce the driving force for grain boundary motion, leading to improved microstructural stability and resistance to deformation. Inclusion of dopants has been shown to alter properties of nanocrystalline materials, although their precise effect on mechanical and electrical properties is still unclear. In this brief review article, work done in the domain of stability of polycrystalline materials using dopants and their application in nanocrystalline materials is discussed. The importance of both experiment and molecular dynamics simulations is presented.

Keywords: nanocrystalline materials; dopants; thermal stability; stress assisted; grain growth

1. Introduction

Over the past decade, new nanocrystalline and/or nanostructured materials with key microstructural length scales on the order of a few tens of nanometers have emerged. Nanocrystalline materials have unique properties as compared to their microcrystalline counterparts, including increased strength [1]. Due to their unique properties, these materials have the potential to revolutionize several industries that depend on high performance materials. For example, miniaturization of electronic devices using interconnects with pitch less than 50 μm can be made possible using nanocrystalline copper interconnects [2].

Nanocrystalline materials are three dimensional solids with average grain size <100 nm and are either single phase or multi-phase. Due to the reduced grain size, a large fraction of atoms are located at the grain boundaries and are displaced relative to their ideal lattice points. As a result, these materials have unique properties that are more representative of the grain boundary surface characteristics rather than properties of the bulk. Deformation in microcrystalline materials is accommodated by nucleation and movement of dislocations within the grains. Dislocations continue to move until they encounter a barrier to their motion, such as a grain boundary, resulting in the formation of dislocation pile-ups. In nanocrystalline materials, dislocation pile-ups and dislocation multiplication via Frank-Read sources within the grains are limited due to the smaller grain size. This increased resistance leads to increases in mechanical strength, σ, via the reduction in the grain size, d, and is characterized by the Hall-Petch relation [3,4],

$$\sigma = \sigma_0 + kd^{-1/2} \tag{1}$$

In Equation (1), σ_0 and k are material specific constants. Experimental results by Weertman [5] and Choksi *et al.* [6] have verified improvement in mechanical properties via the reduction in grain size. The Hall-Petch relation remains valid down to a critical grain size, below which grain boundary processes such as grain boundary sliding become dominant and the strength of the material starts to decrease. This effect is known as the inverse Hall-Petch effect [7,8]. To exploit the superior properties of nanocrystalline materials, it is essential that we operate in a grain size regime that exceeds the size at which the inverse Hall-Petch relationship comes into play and simultaneously in a temperature regime that allows the microstructure to remain stable when placed in service. Unfortunately, materials with nanometer grain sizes are prone to grain growth at temperatures substantially below those at which grain growth occurs in microcrystalline materials [9]. In addition, it has been observed that stress can trigger grain growth in nanocrystalline materials [10]. The mechanism for grain instability and grain growth in nanocrystalline materials is not clearly understood [11]. Thus, one of the current challenges is to produce stable

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ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020701730427
http://www.informaworld.com

nanostructures which do not evolve at elevated temperatures and subsequently do not lose properties during service. To develop techniques to prevent grain growth, it is important to understand the effect of stress and temperature on the microstructure. Continuum theory based models fail at low grain sizes (<100 nm) and new models for plasticity, grain growth and dislocation activity need to be developed [12].

2. Influence of temperature

Due to the increased fraction of grain boundaries in nanocrystalline materials (which have a higher free energy than that of the bulk) there is a greater tendency for grain growth than in microcrystalline materials. Via a thorough understanding of the role of grain boundary geometry and chemical potential of the grain boundary atoms, it is possible to better understand the abnormal grain growth phenomenon.

There is overwhelming evidence of room temperature grain growth in nanocrystalline materials including Cu, Ag, and Pd [9,13–15]. Room temperature grain growth studies of electrodeposited nanocrystalline copper conducted by Pantleon *et al*. [16] showed greater stability for thinner films. A summary of their results is shown in Figure 1. It was found that the fraction of low angle grain boundaries ($<15°$) increased with decreasing thickness of the film. Recent molecular dynamics (MD) simulations on Cu bicrystals by Spearot *et al*. [17] verified that low angle grain boundaries are low energy configurations and generally more stable as compared to high angle grain boundaries. However, it is also observed that depending on the interface misorientation, several high-angle boundaries may have very low energies as well, such as the $\Sigma 3$ (111) symmetric tilt interface.

Bansal [18] has conducted thermal stability tests of nanocrystalline Cu and Ni produced by equal channel angular extrusion (ECAE) up to 250°C. Ni was shown to be stable even at 250°C whereas considerable grain growth was observed in Cu at temperatures >100°C. From these studies the activation energy of Cu and Ni were calculated to be 33 kJ/mol and 55 kJ/mol, respectively. Similar activation energies (30 ± 9 kJ/mol) for grain growth in fully dense nanocrystalline Cu have been reported by Ganpathi *et al*. [19]. By comparison, the activation energy for grain growth of ECAE microcrystalline copper is 80–100 kJ/mol, which is greater than that for nanocrystalline copper [20,21]. *In-situ* XRD measurements of grain growth of nanocrystalline Fe by Natter *et al*. [22] demonstrated that the lower activation energy for grain growth in nanocrystalline materials is attributed to the lower activation energy of diffusion of atoms along the grain boundary and the contention that in nanocrystalline materials, even the bulk phenomena are dominated by the

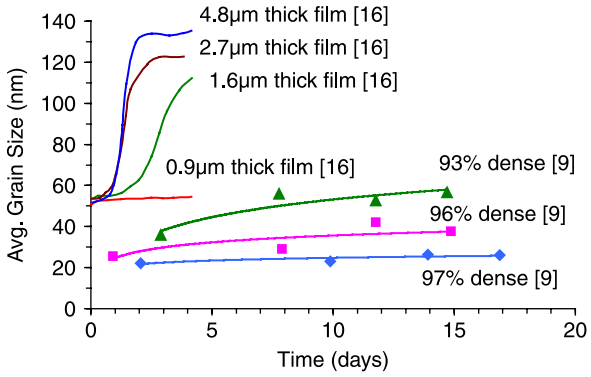

Figure 1. Effect of film thickness [16] and density of sample [9] on grain growth (recrystallization) of Cu at room temperature. No grain growth was observed for film thickness ≤ 0.4 μm.

grain boundaries. Similar results of enhanced grain boundary diffusivity in nanocrystalline Fe have been observed by Tanimoto *et al*. [23]. Recent thermal stability tests on ECAE pure copper by Molodova *et al*. [24] also indicated that the grain growth rate and activation energy were found to be a function of the grain size and number of passes during ECAE. Grain growth was triggered at lower temperatures for decreasing grain size and increasing number of ECAE passes. Also, the fraction of high energy grain boundaries was shown to increase with the number of passes and is a probable cause for the greater instability.

Grain boundary mobility, m, is defined as the grain boundary velocity per unit pressure [25]. The dependence of grain boundary mobility on the diffusivity within the grain boundary, D_{gb}, under the influence of a driving force is described by [26],

$$m = \left(\frac{a^2}{kT}\right) D_{gb}. \tag{2}$$

Here, a is the lattice parameter, k is Boltzmann's constant and T is the absolute temperature, According to Equation (2), it is possible to suppress grain boundary mobility by decreasing D_{gb} thus preventing grain growth. The diffusivity within the grain boundary, D_{gb}, is an exponential function of the activation energy for diffusion, Q, and temperature [27],

$$D_{gb} = D_0 \exp\left(-\frac{Q}{RT}\right). \tag{3}$$

Here, D_0 is the material specific diffusivity constant and R is the gas constant. According to Equations (2) and (3), the intrinsic mobility can be reduced by increasing the activation energy for diffusion along the grain boundary thus preventing grain growth.

Experimental results by Gertsman *et al*. [9] showed that grain growth of nanocrystalline Cu at room

temperature depends on the density of the sample, as illustrated in Figure 1. Less dense samples were found to be more unstable. The pores in the samples act as paths for surface diffusion thereby increasing self-diffusion in the grains and causing greater instability [23]. From the above discussion it is clear that it is possible to improve thermal stability of the microstructure by reducing grain boundary self-diffusion, the fraction of high energy grain boundaries and by preparing fully dense samples.

3. Influence of stress

Stress assisted grain growth has been recently studied in nanocrystalline materials via both experiment and molecular dynamics simulations. Bansal [18] observed grain growth in nanocrystalline copper after conducting low cycle fatigue tests using a loading ratio, $R = -1$. The average grain size increased from 45 to 58.5 and 72.0 nm at strains of 1.0 and 1.5%, respectively, indicating stress driven grain growth. To elucidate the influence of stress on grain growth behavior, nanoindentation studies were carried out by Zhang *et al*. [10] at cryogenic temperatures (−190°C). Such tests at very low temperatures suppress thermal and diffusion effects, thus, grain growth observed was purely stress driven. Furthermore, in creep experiments conducted using nanocrystalline copper, Bansal [18] observed a threshold stress required for grains to grow at a given temperature.

Certain stress driven grain growth mechanisms have been explained using both experiments and simulations. Zhang *et al*. reported that grain rotation and coalescence were the primary grain growth mechanisms due to the large number of low angle grain boundaries in the vicinity of indentations in nanocrystalline copper at −190°C [10,28]. Schoitz [29] studied behavior of nanocrystalline materials under cyclic loading (10% strain, $R = -1$) using molecular dynamics simulations. He reported that the mechanisms for stress assisted grain growth can be explained by grain rotation and grain coalescence. However, Sansoz and Dupont [30] used multi-scale simulations of nanoindentation at 0 K to show that grain growth mechanisms in nanocrystalline materials are primarily due to grain rotation and the migration of unstable grain boundaries. Haslam *et al*. [31] studied grain growth in nanocrystalline Pd microstructures using MD simulations at 1200 K under the influence of stress and compared it with the stress-free configuration. Grain growth was observed only under the influence of stress due to increased diffusion of atoms at the grain boundary. The mechanism for the observed stress assisted grain growth was curvature driven grain boundary migration and by grain rotation-induced grain coalescence. Supplemental simulations performed at 1400 K without any external stress showed grain growth by similar mechanisms but the intensity of growth was suppressed in the absence of external stress.

It is suggested that the presence of extrinsic grain boundary dislocations [26] and the emission of free dislocations from the interface [32] are critical for stress induced grain growth by facilitating grain boundary migration. Hence presence of high energy non-equilibrium grain boundaries in nanocrystalline materials makes them more susceptible to stress assisted grain growth. Recent studies by Lu *et al*. [33] on electro-deposited and cold-rolled nanocrystalline copper provided the experiment verification of this argument. In their work, final microstrain and grain size were measured after both materials were annealed for fixed time at different temperatures (see Figure 2). It was observed that in both samples, grain growth was triggered at approximately the same temperature at which the internal microstrain is relieved. This result provided (i) a relationship between internal microstrain and grain growth in nanocrystalline materials and (ii) further validation that stress can assist grain growth.

From the above discussion it is understood that grain growth can be prevented by eliminating grain rotation and the non-equilibrium grain boundaries. However as per our knowledge, there is no theory yet to fully explain stress induced grain growth.

4. Role of dopants

One potential method to prevent grain growth is by eliminating grain boundary mobility (sliding or migration). The grain boundary migration rate, V, depends on the driving force, P, and intrinsic mobility, m, [26],

$$V = mP^n \text{ (usually } n = 1) \tag{4}$$

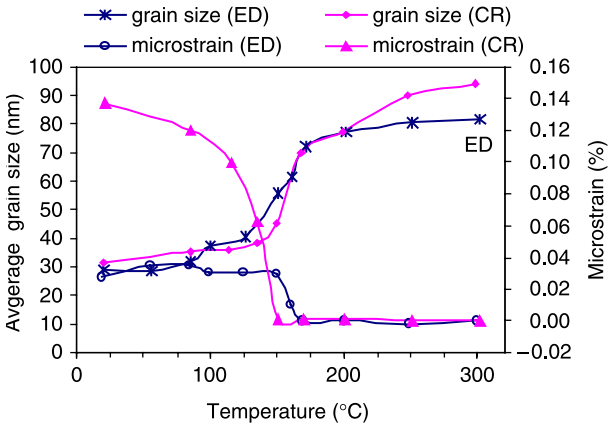

Figure 2. Grain growth is initiated in cold rolled (CR) and electrodeposited (ED) copper nanocrystalline copper at about the same temperatures at which stress relief occurs [33].

Presence of dopant atoms alters the grain boundary kinetics and induces a "solute-drag" effect [26]. Thus, the presence of dopants atoms could reduce the driving force for grain boundary migration, thereby suppressing grain growth. From Equation (2), a decrease in mobility will also lead to decrease in diffusion within the grain boundary which is the primary mechanism for room temperature grain growth in nanocrystalline materials.

Furthermore, the theoretical stress approach by Li [32] indicated that the two main conditions required for stress assisted grain growth are (i) metastable or high energy grain boundary structure (ii) high purity material. Increase in the number of free (non-equilibrium) dislocations in homogeneous grain boundaries reduces the shear stress required for their emission as shown in Figure 3 (provided that they are slip compatible with the opposing lattice regions) thus facilitating stress assisted grain growth. The number of free dislocations can be reduced by pinning them within the grain boundary using segregated dopant atoms, thereby increasing the magnitude of stress required for grain growth.

Another approach that has been proposed to control grain growth is to suppress the thermodynamic driving force for grain migration [34]. Greater fraction of high energy grain boundaries in nanocrystalline materials makes them more susceptible to grain growth as compared to their polycrystalline counterparts. Specifically, grain growth can be suppressed thermodynamically by driving the excess grain boundary energy, γ_{GB}, to zero. This can be achieved by introducing dopants at the grain boundaries, the effect of which is characterized by [35],

$$\gamma_{GB} = \gamma^0_{GB} - \Gamma_{dop}\,(RT \ln X_0 + \Delta H_{seg}) \qquad (5)$$

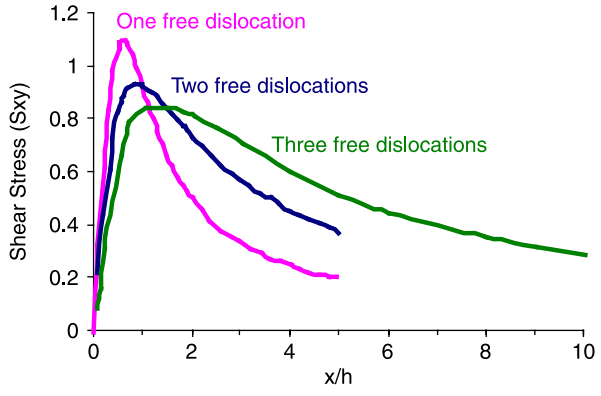

Figure 3. Decrease in shear stress required with increasing number of free dislocations at a tilt grain boundary. Thermal effects are not considered in this model (x is the distance of free dislocation from center of grain boundary and h is the spacing between dislocations) [32].

In Equation (5), γ^0_{GB} is the grain boundary energy of a pure solvent (homogeneous interface), Γ_{dop} is the dopant coverage on grain boundary, X_0 is the bulk solute concentration, ΔH_{seg} is the excess enthalpy change of segregation per mole of solute. Equation (5) indicates that the grain boundary potential energy can be decreased by increasing the dopant concentration and coverage along the grain boundary, thereby eliminating the thermodynamic drive for grain growth. By eliminating the driving force, i.e. the excess grain boundary energy, the grain boundary mobility will decrease as per Equation (4). However, note that this theory applies to dopants that segregate to the grain boundary and do not form precipitates [36]. Recent molecular dynamics simulations by Millett *et al*. [37,38] further bolsters the theory that presence of atoms larger than host atoms at the grain boundary can reduce γ_{GB} to zero. Specifically, Millett *et al*. concluded (i) that the concentration of dopant atoms (Γ_{dop}) needed to lower γ_{GB} and prevent gain growth is a function of relative size of dopant atoms, r_{dop}/r_{host} (r_{dop} and r_{host} are the radius of dopant and host matrix atoms respectively) and (ii) that grain boundary energy is not influenced by the cohesive energy of dopant atoms but strongly depends upon the relative size of dopant atoms. Recent MD studies of nickel doped with tungsten showed that the grain boundary energy did not become zero for any tungsten composition [39]. However, it is to be noted that the solubility of *W* in Ni is significant (12% at room temperature) and the thermodynamic model for the reduction in brain boundary energy (Equation (5)) may not be applicable.

The general observations reported by MD simulations have been validated via experimental studies of metastable nanocrystalline materials. Researches have used solid dopants ($Pd_{100-x}Zr_x$ [34], $Y_{100-x}Fe_x$ [40], Cu-0.2 wt% B [41]) and gaseous impurities (Ag-7 at% O [15]) to improve microstructural stability. Krill *et al*. [34] and Weissmuller [40] increased the solute concentration and were able to prevent grain growth up to a certain temperature. Nanocrystalline Cu–Nb alloy (10 at% Nb) prepared by mechanical alloying was observed to be stable up to 900°C [42]. However in their work, at higher powder consolidation temperatures, large (~90 nm) Nb precipitates form, resulting in a significantly negative impact on electrical conductivity (~90% international annealing Cu standard).

Due to the increased fraction of grain boundaries in nanocrystalline Cu, the electromigration rate is expected to increase thereby creating reliability issues. It has been shown by Gutmann *et al*. [43] that electromigration resistance of Cu decreases significantly by adding small (~1%) amount of dopants at grain boundaries without increasing the electrical resistance appreciably. This dopant concentration is commensurate with that needed

to drive grain boundary energy to zero as shown by Millett *et al*. [37,38].

5. Conclusions

It is important to fully understand the kinetics and mechanisms associated with grain growth in nanocrystalline materials under the influence of stress and temperature. These mechanisms have been shown to be dependant on the processing or deformation procedures, making it difficult to compare data in the literature. Both simulation and experiment have shown that dopants may be used to produce stable nanocrystalline materials. Further experimental and computational research needs to be conducted to determine (i) how to successfully drive dopant atoms to grain boundaries during processing and (ii) what affect dopant atoms at the grain boundaries have on other functional properties of the material.

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