Influence of Stress and Temperature on the Microstructure Stability of Nanocrystalline Materials

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ABSTRACT

It is well established that nanocrystalline materials have unique mechanical and electrical properties in comparison to their microcrystalline counterparts due to their reduced crystallite or grain size. 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 crystalline 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, grain growth.

1 INTRODUCTION

Over the past decade, new nanocrystalline and/or nanostructured materials with key microstructural length scales on the order of 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 height less than 65 nm can be made possible using nanocrystalline copper interconnects produced by an equal channel angular extrusion (ECAE) technique [2].

Nanocrystalline materials are three dimensional solids with average grain size <100 nm and are either single phase or multi-phase. The improvement in mechanical properties in nanocrystalline materials is attributed to the reduction in crystallite grain size leading to a larger percentage of atoms being located in the interfacial regions and grain boundaries than at lattice points. Deformation in polycrystalline 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],

$$\sigma = \sigma_o + kd^{-1/2} \quad . \tag{1}$$

In Eq. 1, σ_o and k are material specific constants. Experimental results by Weertman [5] and Bansal et al. [6] have verified improvement in mechanical properties by reduction in grain size down to a critical grain diameter. Unfortunately, materials with nanometer grain sizes are prone to grain growth at temperatures substantially below those at which grain growth occurs in microcrystalline materials [7]. In addition, it has also been observed that stress can trigger grain growth in nanocrystalline materials [8]. The mechanism for grain instability and growth in nanocrystalline materials is not clearly understood [9]. Thus, one of the current challenges is to produce stable nanostructures whose microstructures 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 of plasticity, grain growth and dislocation structure need to be developed [10].

2 INFLUENCE OF TEMPERATURE

Due to the increased volume 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, Pd [7, 11-13]. Room temperature grain growth studies of electrodeposited nanocrystalline copper conducted by Pantleon et al. [14] show greater stability for thinner films (Fig. 1). It was found that the fraction of low angle grain boundaries (<15°) increased with decreasing thickness of the film. Recent molecular dynamics simulations on Cu bicrystals by Spearot et al. [15] 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 Σ3 (111) symmetric tilt interface.

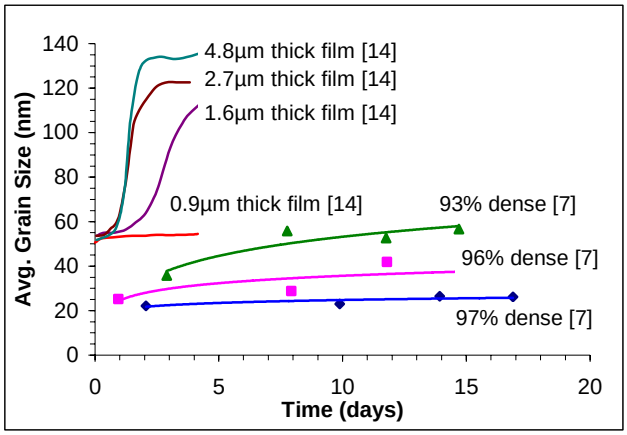

Figure 1: Effect of film thickness [14] and density of sample [7] on grain growth (recrystallization) of Cu at room temperature. No grain growth was observed for film thickness ≤ 0.4μm.

Bansal [16] conducted thermal stability tests up to 250 °C using nanocrystalline copper and nickel produced by ECAE. Nickel was found to be stable up to 250 °C whereas considerable grain growth was observed in copper at temperatures >100 °C. Interestingly, the grain growth activation energies in these tests were calculated as 33 KJ/mol and 55 KJ/mol for copper and nickel respectively, lower than their microcrystalline counterparts as a result of the lower grain boundary self-diffusion energy in nanocrystalline materials [17]. The dependence of grain boundary mobility, m, on the diffusivity within the grain boundary, D_{gb}, under the influence of a driving force is described by [18],

$$m = (a^2 / kT) D_{gb} \quad . \qquad (2)$$

Here, a is the lattice parameter, k is Boltzmann's constant and T is the absolute temperature. Equation 2 implies that it is possible to suppress grain boundary mobility by decreasing D_{gb} thus preventing grain growth.

3 INFLUENCE OF STRESS

Stress assisted grain growth has been recently studied in nanocrystalline materials via both experiment and molecular dynamics simulations. Bansal [16] 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 nm to 58.5 nm 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. [8] at cryogenic temperatures (-190 °C). Such tests at very low temperatures suppress thermal and diffusion effects, thus, grain growth observed was purely stress driven. Also, in creep experiments conducted using nanocrystalline copper, Bansal [16] observed a threshold stress required for grains to grow at a given temperature.

Various 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 [8, 19]. Schoitz [20] 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 et al. [21] used multi-scale simulations of nanoindentation at ~0K to show that grain growth mechanisms in nanocrystalline materials are mainly grain rotation and the migration of unstable grain boundaries.

It is suggested that the presence of extrinsic grain boundary dislocations [18] and the emission of free dislocations from the interface [22] 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. [23] on electrodeposited and cold-rolled nanocrystalline copper provide 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 (Fig. 2). Due to higher microstrain in cold-rolled copper, it was found to be more unstable and grain growth began at a lower temperature as compared with the electrodeposited copper. These results indicate that the presence of high energy grain boundaries (which is evident from the higher average microstrain) induce greater instability.

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, via [18],

$$V = mP^n \quad (\text{Usually } n = 1) \quad . \tag{3}$$

According to Eq. 3, presence of dopants (impurities) could reduce the driving force for grain boundary migration, thereby suppressing grain growth. Presence of dopant atoms alter the grain boundary kinetics and induce a 'solute-drag' effect [18]. From Eq. 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.

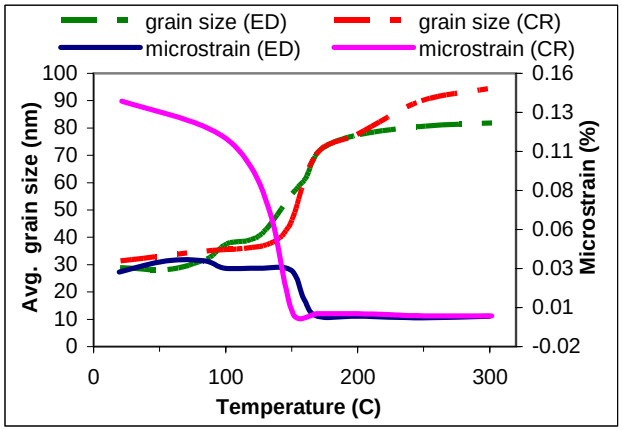

Figure 2: Cold rolled (CR) nanocrystalline copper with higher residual microstrain begin to anneal at lower grain size and lower temperature as compared to electrodeposited (ED) copper [23].

Furthermore, the theoretical stress approach by Li [22] indicates 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 Fig. 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 [24]. 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 [25],

$$\gamma_{GB} = \gamma^o_{GB} - \Gamma_{dop}(RT \ln X_o + \Delta H_{seg}) \quad . \tag{4}$$

In Eq. 4, γ^o_{GB} is the grain boundary energy of a pure solvent (homogeneous interface), Γ_{dop} is the dopant coverage on grain boundary, X_o is the bulk solute concentration, ΔH_{seg} is the excess enthalpy change of segregation per mole of solute, r_{dop} and r_{host} are the radius of dopant and host matrix atoms respectively.

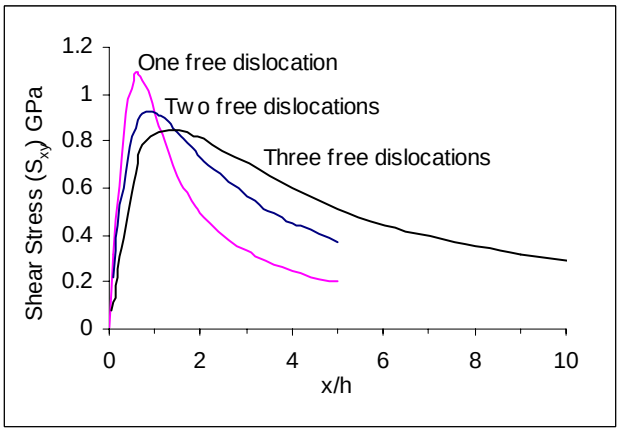

Figure 3: Decrease in shear stress required with increasing number of free dislocations at a tilt grain boundary. Thermal effects are not considered in this model (x is the distance of free dislocation from center of grain boundary and h is the spacing between dislocations) [22].

Eq. 4 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. However, note that this theory applies to dopants that segregate to the grain boundary and do not form precipitates [26]. Recent molecular dynamics simulations by Millett et al. [27, 28] 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. conclude:

- 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}).

- Grain boundary energy is not influenced by the cohesive energy of dopant atoms but strongly depends upon the relative size of dopant atoms.

The general observations reported by MD simulations are also made via experimental studies of metastable nanocrystalline materials. Researches have used solid dopants ($Pd_{100-x}Zr_x$ [24], $Y_{100-x}Fe_x$ [29], Cu-0.2 wt% B [30]) and gaseous impurities (Ag-7 at% O [13]) to improve microstructural stability. Krill et al. [24] and Weissmuller [29] 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 ^oC. 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).

5 CONCLUSIONS

It is important to fully understand the kinetics and mechanism of 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 literature. Both simulation and experiment have shown that dopants may be used to produce stable nanocrystalline materials. Further experimental 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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