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Atomistic Simulation Studies Of Grain-Boundary Segregation And Strengthening Mechanisms In Nanocrystalline Nanotwinned Silver-Copper Alloys

Xing Ke

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ATOMISTIC SIMULATION STUDIES OF GRAIN-BOUNDARY SEGREGATION
AND STRENGTHENING MECHANISMS IN NANOCRYSTALLINE
NANOTWINNED SILVER-COPPER ALLOYS

A Dissertation Presented

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Xing Ke

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of

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ABSTRACT

Silver (Ag) is a precious metal with a low stacking fault energy that is known to form copious nanoscale coherent twin boundaries during magnetron sputtering synthesis. Nanotwinned Ag metals are potentially attractive for creating new interface-dominated nanomaterials with unprecedented mechanical and physical properties. Grain-boundary segregation of solute elements has been found to increase the stability of interfaces and hardness of nanocrystalline metals. However, heavily alloying inevitably complicates the underlying deformation mechanisms due to the hardening effects of solutes, or a change of stacking fault energies in Ag caused by alloying. For the above reasons, we developed a microalloying (or doping) strategy by carefully selecting Cu as the primary impurity—a solute that is predicted to have no solid-solution strengthening effect in Ag when its content is below 3.0 wt.%. Neither will Cu affect the stacking fault energy of Ag at a concentration <1.0 wt.%. Moreover, Cu atoms are ~12% smaller than Ag ones, and Ag-Cu is an immiscible system, which facilitates the segregation of Cu into high-energy interface sites such as grain-boundaries and twin-boundary defects. In this thesis, large-scale hybrid Monte-Carlo and molecular dynamics simulations are used to study the unexplored mechanical behavior of Cu-segregated nanocrystalline nanotwinned Ag.

First, the small-scale mechanics of solute Cu segregation and its effects on incipient plasticity mechanisms in nanotwinned Ag were studied. It was found that solute Cu atoms are segregated concurrently to grain boundaries and intrinsic twin-boundary kink-step defects. Low segregated Cu contents (< 1 at.%) are found to substantially increase twin-defect stability, leading to a pronounced rise in yield strength at 300 K. Second, atomistic simulations with a constant grain size of 45 nm and a wide range of twin boundary spacings were performed to investigate the Hall-Petch strength limit in nanocrystalline nanotwinned Ag containing either perfect or kinked twin boundaries. Three distinct strength regions were discovered as twin boundary decreases, delineated by normal Hall-Petch strengthening with a positive slope, the grain-boundary-d dictated mechanism with near-zero Hall-Petch slope, and twin-boundary defect induced softening mechanism with a negative Hall-Petch slope. Third, by systematically studying smaller grain sizes, we find that the “strongest” size for pure nanotwinned Ag is achieved for a grain size of ~16 nm, below which softening occurs. The controlling plastic deformation mechanism changes from dislocation nucleation to grain boundary motion. This transition decreases to smaller grain sizes when Cu contents are segregated to the interfaces. Our simulations show that continuous Hall-Petch strengthening without softening, down to grain sizes as small as 6 nm, is reached when adding Cu atoms up to 12 at. %. For Cu contents ≥ 15 at. %, however, the predominant plastic deformation mechanism changes to shear-band induced softening.

The present thesis provides new fundamental insights into solute segregation, and strengthening mechanisms mediated by grain boundaries and twin boundaries in face-centered cubic Ag metals, which is expected to motivate experimental studies on new nanotwinned metals with superior mechanical properties controlled by microalloying.
CITATIONS

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CHAPTER 1: INTRODUCTION

1.1 Background on Nanotwinned Materials

1.1.1 Nanotwinned Metals

A coherent twin boundary (TB) is a perfectly crystalline interface with high order and symmetry commonly existing in face-centered-cubic (FCC) and body-centered-cubic (BCC) metals or ceramics. Nanotwinned (nt) materials are composed of coherent TBs with nanometer-scale spacing. TBs can form in materials with low to medium stacking fault energy during growth, deformation or annealing [1-3]. Nt-Cu has been extensively studied in the past. The tensile strength of nt-Cu is one order of magnitude larger than its coarse-grained counterpart with comparable electric conductivity.

Coherent TBs have low excess energy and are a better choice for strengthening materials compared with standard grain boundaries (GBs). GBs are incoherent and more disordered [4-7].

Figure 1. 1 (a) displays the transmission electron microscopy (TEM) image of as-grown nt-Cu obtained by electrodeposition [5]. The average grain size is shown to be around 400 nm and twin size is several nanometers, as shown in Figure 1(b) and (c), respectively. Closeup images of the nanoscale TB packing are shown in Figure 1 (d)-(e).
Figure 1.1: Microstructure of electrodeposit ed nanotwinned Cu. (a) TEM image and electron diffraction image. (b) Statistical analysis of grain size. (b) Statistical analysis of twin size. (d) Electron diffraction showing parallel twins. (e) Close-up image of twin atomic structure adapted from [4].

Studying dislocation activities using classical molecular dynamics (MD) simulations is an essential approach to understand the deformation process and provides us with clues to understand the strength and plasticity of materials at the atomic scale. Strengthening in nt metals results from the blockage of dislocation motion by TBs. You et al [8] have studied the anisotropy in plasticity in columnar-grained nt-Cu with preferentially oriented nanoscale twins and identified three distinct dislocation-based deformation mechanisms as shown in Figure 1.2. For twin size \( \lambda \) larger than 100 nm, dislocation-dislocation interaction is dominant, and the strength is insensitive to loading directions. For \( \lambda \) below 100 nm, the deformation mechanism is dependent on the relative TB angles with respect to the loading direction: confined threading dislocation inside twins is dominant at 0°; TB migration from partial dislocation motion at 45°;
dislocation pile-up and cutting through TBs at 90°. A strong anisotropy in yield strength and strain hardening is thus observed in this type of materials.

![Diagram](image)

**Figure 1.2: Deformation-mechanism map for nanotwinned metal with respect to different loading directions adapted from [8].**

The effect of introducing TBs can result in either softening or strengthening depending on specific materials and deformation mechanisms. Nt-Cu and Nt-Pd have been studied theoretically by atomistic simulations [9]. Nt-Cu shows hardening effects due to the presence of nanotwins, while nt-Pd shows softening. For nt-Cu, dislocations nucleate from slip system with high Schmid factors and are blocked by TBs. For nt-Pd, dislocations are restricted to TB planes. TB migration leads to softening.
1.1.2 Twin Defects in Nanotwinned Materials

CTBs were considered perfect, but recent study of high-resolution TEM inverse-pole-figure-orientation mapping (IPFOM) showed the existence of defective, incoherent, kink-like segments on TBs for nt-Cu as shown in Figure 1.3 [10]. Magenta and purple part in the figure show the twins with different orientations, separated by CTBs marked in red color. Deformation mechanisms are affected by the kinks since those defects can migrate during deformation, react with nearby kinks, act as potential positions for dislocation nucleation and interact with other dislocations from GBs.

The atomic structure of each kink step was equivalent to repeating pattern $b_2:b_1:b_3$ of an incoherent $\Sigma 3\{112\}$ TB, with Burgers vectors $b_1=1/6[\overline{1}12]$, $b_2=1/6[\overline{2}1\overline{1}]$ and $b_3=1/6[2\overline{1}1]$, characterized by a zero sum [11].

![Shift of two twin planes](image)

Figure 1.3: High resolution image of inverse pole figure orientation mapping (IPFOM) showing microstructure of nanotwinned Cu with kink-step like defects adapted from [10].

MD simulations in this work identified several new kink-dependent deformation mechanisms; for example, partial dislocations and kink defects pinning interaction,
dislocation nucleation from kink-GB interactions, detwinning of kink defects, twinning partial emission from kink defects. These simulations have proven that the strengthening and softening mechanisms are fundamentally influenced by the presence of kink-steps on TBs.

Figure 1. Molecular dynamics simulations of deformation mechanisms in columnar-grained nanotwinned Cu with kink defects at strain (a) 0%. (b) 1.7%. (c) 5%. M: migrating kink defects. P: partial dislocation from GB. L: Lomer lock adapted from [10].

The interaction between dislocations and defective TB containing intrinsic kink-step defect has been studied later in nanotwinned copper bicrystal using molecular dynamics simulation [12]. It was found the strengthening effect from defective TBs is observed at medium to high applied strain.
At low applied strain, dislocation absorption at TBs is prevailing but no hardening was observed. At medium to high applied strain, the deformation mechanism changes from direct dislocation transmission to dislocation absorption, which resulted in a pronounced rise in strain hardening. Dislocation pinning by kink steps was also observed for 60-degree intersection as shown in Figure 1.5.

1.1.3 Hall-Petch Effect

The Hall-Petch strengthening, or GB strengthening, [13, 14] describes the relation between materials strength and average grain size, which is given by equation:
\[ \sigma = \sigma_0 + \frac{K}{\sqrt{d}} \]  

(1.1)

where \( \sigma \) is the flow strength, \( \sigma_0 \) is friction stress, \( K \) is the Hall-Petch constant and \( d \) is the average grain size. This relation shows that decreasing \( d \) increases material strength. However, when the grain size is reduced to nanometer range, a softening behavior has been observed [15]. The softening effect below strongest grain size in nanocrystalline (nc) Cu was first simulated using MD in [16] as shown Figure 1.6. The simulated stress-strain curves are shown in Figure 1.6 (a). The softening is observed when grain size decreases. Yields stress and flow stress are summarized in Figure 1.6 (b) and (c). By atomic-scale analysis, it was found that the softening resulted from dominant interface sliding events inside GBs instead of dislocation propagation inside the grains.

![Figure 1.6](image)

Figure 1. 6: The effect of grain size on deformation and the reverse Hall-Petch effect in nc-Cu. (a) Simulated stress-strain curves at different grain sizes. (b) Flow stress. (c) Yield stress adapted from [16].

The concept of a “strongest size” was first brought up by S. Yip [17] to describe the critical grain size at which the softening transition occurs and maximum strength is
achieved. Above the strongest size, dislocation pile-up was suggested as the controlling deformation mechanism following the Hall-Petch relation. Below the strongest size, interface deformation by GB sliding, GB migration and grain rotation, play a more important role leading to softening.

Figure 1. 7: “Strongest size” concept. (a) Definition of the strongest size from Yip 1998. (b) Molecular dynamics simulations of nc-Cu adapted from [19].

For nc-Cu metals up to 50 nm simulated in [18] and [19], the maximum in the flow stress was theoretically predicted to be around a grain size of 10 nm to 15 nm. The deformation mechanism shifted from dislocation-mediated plasticity at large grain size to GB sliding at smaller grain sizes. H. Conrad et al. have studied the relationship between flow stress and grain size in Cu with larger grain size ranges [20, 21]. Three regimes were observed. For grain size larger than 1000 nm, dislocation cells were formed during deformation; for grain size between 10 nm and 1000 nm, dislocation were restricted to slip planes; for grain size smaller than 10 nm, softening is observed. Analysis were done for other metals, Niobium [22], Zinc [23], and Silver [24] with similar trends. The Hall-Petch relation was derived by assuming that GBs contained
Frank-Read sources that could pin dislocation motion [25]. This model was supported by experimental data of Cu, Pd, Ni, NiP and Fe summarized by Lian et al. [26]. The strongest size has been systematically studied on different metals using molecular dynamics simulations, nc-Al [21], nc-Mg [27], nc-Ni [28]; or transmission electron microscopy of nc-Pt films [29]. Pure nc-metals always show an inevitable softening below a critical grain size.

1.1.4 Twin Size Effect

The strongest size was also shown to apply to twin size effects in nt-Cu [30]. Samples with a grain size between 400 nm to 600 nm were prepared with different twin sizes. As twin size decreases, the strength of nt-Cu increases following a Hall-Petch relation similar to the strengthening effect from GBs. The maximum strength was found for twin size $\lambda = 15$ nm. Below the strongest twin size, a softening behavior was observed due to deformation mechanism changing from slip transfer across TB to the activity of pre-existing easy dislocation sources.

The deformation mechanisms were further studied [31] by computer simulations (Figure 1.8). A Hall-Petch effect exists for large TB spacing due to dislocation pile-up and cutting through twin planes.
Figure 1.8: Strongest size and deformation mechanisms in nanotwinned Cu. (a) Maximum yield strength for TB is found when $\lambda = 15$ nm, experimentally [30]. (b) MD simulations of parallel dislocations for $\lambda = 1.25$ nm model at 7 % applied strain, and (c) Intersecting dislocations for $\lambda = 6.25$ nm model at 5.4 % applied strain adapted from [31].

For smaller twin sizes ($\lambda \leq 1.25$ nm in Figure 1.8 (b)), the deformation mechanism shifts to dislocation-controlled softening resulting from the nucleation and motion of partial dislocation parallel to the twin planes. The dislocation sources are located at GB-TB triple junctions [32]. Therefore, the strongest twin size is also dependent on the grain size. Smaller grain size model reaches maximum strength with smaller twin size.
Strain gradient theory was applied to explain the plastic deformation at micron and submicron length scales [33] by introducing geometrically necessary dislocations into the Taylor hardening relation. The theory was further used to describe the dislocation pile-up zone around GB and TB in nt-metals [34]. For nt-Cu with 500 nm grain size, the strongest twin size was estimated to be 13 nm, which is in good accordance with experimental results from work in [30].

1.2 Background on Solute Segregation Strengthening

1.2.1 Segregation Effect on Strength

Solute atoms segregation during alloying is an effective approach to increase thermal stability and mechanical strength in metals. Proper choice of a solute atom could effectively induce GB segregation and reduce the GB free energy. Also, precipitates can be formed around GBs at larger solute contents and possibly have a pinning effect on GBs. A theoretical model based on cohesive energy change during equilibrium segregation has been presented [35]. A GB cohesion map is presented to show whether a solute-solvent pair will exhibit strengthening or weakening on GB. It is shown that strength and thermal stability are increased markedly in polycrystalline Ni segregated with 0.14% Ti [36]. Segregation effect of Nb and Fe on nt-Cu has been studied. Significant hardness increase was observed when introducing GB solute [37]. Zhang et al have shown that segregating Zr atoms to 0.5 at% into nanostructured Cu will increase hardness, tensile ductility and fatigue lifetime to the largest amount [38].
While for Zr content above 2.0 at%, GB doping effect is weakened due to amorphous phase formation. Alloying effect of Zn in nanocrystalline Cu has been studied experimentally. The optimum grain size for deformation twins increases slightly with increasing Zn content [39]. Experimental studies have been applied to mechanically alloyed Cu-Nb system up to 10 at%. Grain growth resistance was found to increase with Nb content. Cu-5%Nb exhibited the highest Vickers hardness 2.5 to 3 times than unalloyed Cu. Because as Nb% increases higher, GB accumulated Nb atoms and thickens into Nb zones leading to phase separation and precipitation [40]. GB doping has been applied to Al-Mg alloys made by mechanical milling and annealing treatments. Mg atoms are segregated to GBs in Al due to high GB segregation enthalpy. Annealed nanocrystalline Al-7 at% Mg reaches a hardness of 4.56 GPa, about 3 times of the pure nanocrystalline Al. Also, the alloy is one of the strongest lightweight metals [41]. All these experimental facts provide evidence that introducing a proper amount of
solute atoms will alter the microstructure of alloys, especially at defective locations, and increase stability and mechanical properties.

Hybrid Monte-Carlo / molecular dynamics (MC/MD) simulations have been applied to nanocrystalline Cu with Ag segregation at different concentrations [42]. In Figure 1.11, as Ag concentration increases, Ag atoms are segregated to the GBs. At high Ag concentration as in Figure 1.11 (c), a thick layer of Ag is formed along the GB distribution. The close-up view of Ag distribution is shown in Figure 1.11 (d) and (e).

Figure 1. 10: Snapshots of Ag distribution inside nanocrystalline Cu with different Ag concentrations. (a) and (b) are models with 15 nm grain size at Ag concentration 1.88, 8.35 Ag atoms/nm$^2$. (c) model with grain size 40 nm at Ag concentration 223.7 Ag atoms/nm$^2$. (d) and (e) show the close-up view of Ag distribution inside GBs. The Cu and Ag atoms are colored in red and black respectively from (a) to (c). Centrosymmetry parameter with scale bar from 0 to 10 is used for (d) and (e), where 0 represent FCC location and a higher value represents more deviation from FCC local structure, namely defects adapted from [42].
The yield stress and flow stress are summarized in Figure 1.12. As solute Ag atoms increases, both yield stress and flow stress will increase, reach maximum and decrease as Ag layer start to form inside the GBs.

![Figure 1.12: (a) 0.2 % offset Yield stress and (b) Flow stress summary of different grain sizes at different Ag concentration adapted from [42].](image)

1.2.2 Segregation Effect on Hall-Petch Behavior

Segregation is also an effective approach to suppress the softening behavior at smaller grain sizes and decreases the strongest size. The nanocrystalline Ni-W alloy showed higher hardness and scratch resistance compared with pure nc-Ni. The breakdown of the Hall-Petch relation was shown to be suppressed by W addition [28]. The relation between strongest size of the Ni-W alloy and the strongest size of the pure Ni is shown in Equation (1.2).

\[
\frac{d_{\text{Ni-W}}}{d_{\text{Ni}}} = \left[ \frac{D_{\text{W}}}{D_{\text{Ni}}} = (1 - c) + c \right]^{2/7}
\]  

(1.2)
where \( d_{\text{Ni-W}} \) is the strongest size in Ni-W alloy, \( d_{\text{Ni}} \) is the strongest size in pure Ni, \( D_W \) diffusivity of W, \( D_{\text{Ni}} \) is the diffusivity of Ni and \( c \) is the concentration of W. The softening of the nanocrystalline Ni-W alloy was further investigated [43].

The maximum strength was found to be around 8 nm, as predicted by [28]. In nc-Ni alloy with Mo segregation, ultrahigh hardness is observed through relaxation in nanograin samples above Hall-Petch slope [44]. In Figure 1.13, increasing GB stability through Mo segregation was shown to be an effective way to increase the strength of nanocrystalline Ni at grain sizes below 10 nm, where softening is observed for pure samples.

![Figure 1.12: Hardness of Ni and Ni-Mo alloys of different grain sizes adapted from [44].](image)
1.2.3 Nanotwinned Silver-Copper Alloys

Silver (Ag) is a precious metal widely used in electronics, photography, jewelry, and silverware. Ag has low stacking fault energy ~16 mJ·m⁻² [45] and is known to form copious growth nanotwins during magnetron sputtering processes [46, 47]. The smallest grain sizes achieved using this method is ~150 nm [47].

Figure 1.13: TEM cross-sectional images for samples taken from C1 position for (a) 100 W (1.8 nm/s), (b) 175 W (3.2 nm/s) and (c) 300 W (5.4 nm/s) films adapted from [47].

Heavy-alloying is a common approach to decrease the grain sizes but the fundamental strengthening mechanism can change due to different solutes[48], for example, precipitation formation or change of stacking fault energy. Thus the microalloying approach is applied by carefully selecting Cu as the primary solute element. Our own simulation suggested Cu have no effect on solid-solution strengthening effect in Ag when its content is below 5 at. % and neither effect on
stacking fault energy at 1.5 at.%. Moreover, Cu atoms are ~12% smaller than Ag and Ag-Cu is an immiscible system, which facilitates the segregation of Cu into high-energy interface sites such as GBs and TB defects [49].

1.3 Objective of the Dissertation

The objective of this thesis is to use large-scale hybrid MC/MD simulations to study the effects of kink defects, solute segregation, grain size and twin size on the mechanical behavior of nanotwinned Ag, and to provide insight into the underlying plastic deformation mechanisms from a atomistic viewpoint. The objectives can be summarized by asking three main questions. First, how Cu impurity segregation affect the yielding and deformation process of nanotwinned Ag with intrinsic kink-step defects? Second, how different twin sizes affect the strength of pure and Cu-segregated nanotwinned Ag? Third, how different grain sizes affect the strength of pure and Cu-segregated nanotwinned Ag, and at smaller grain sizes, can the Hall-Petch relation be retained by higher Cu segregation?

1.4 Simulation Methods

1.4.1 Molecular Dynamics

Molecular dynamics (MD) is a computational technology to simulate systems composed of atoms or molecules. Using a given interatomic potential, the atoms or molecules interact with each other for a certain timestep and their trajectories are numerically solved. It has been widely applied to materials science to elucidate the
microscopic atom motions, or predict different macroscopic properties, for example, Young’s modulus, simulated stress-strain curve, thermal conductivity, etc. The associated time and length scale of MD simulations [50] is shown together with other simulation methods in Figure 1.15.

![Diagram showing time and length scale range of different simulation methods](image)

Figure 1.14: Time and length scale range of different simulation methods adapted from [50].

A classical MD simulation is carried out in four steps as follows. Step 1: structure generation or model preparation. original coordinates of atoms or molecules are generated based on experimental facts, for example, lattice constants and crystalline structures. Step 2: energy minimization: original generated structures are relaxed by adjusting the atom coordinates in an iteration, which terminates at certain criteria when a local potential energy minimum is found. Starting step 2, the interaction of atoms is constrained by a semi-empirical interatomic potential. In the case of metal simulations,
the embedded-atom method (EAM) potentials are commonly used [51]. The equation to
calculate the total energy of atom i is:

\[
E_i = \Phi \left( \sum_{i \neq j} \rho_j (R_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{ij} (R_{ij})
\]  

(1.3)

where \( \Phi \) is the energy of embedding atom i into the system, \( \rho_j \) represents the
contribution to the electron charge density from atom j, \( R_{ij} \) is the distance between atom
i and j, \( \phi_{ij} \) is the two-body pair-wise function for potential. The force \( F_i \) on atom i can
be calculated using:

\[
F_i = -\nabla E_i
\]  

(1.4)

Step 3: dynamic relaxation: after energy minimization, the atoms in the system
will be assigned with an initial random-generated velocity distribution of an ensemble
and allowed to relax in the ensemble to reach a well-sampled structure with position
and velocity distribution updated regularly each timestep. The Verlet algorithm [51] is
widely used to integrate Newton’s equation of motion. Taylor expansion is used on
atom coordinates \( R(t) \) at time \( t+\Delta t \), and \( t-\Delta t \):

\[
R(t+\Delta t) = R(t) + R'(t)\Delta t + \frac{R''(t)}{2} \Delta t^2 + \frac{R'''(t)}{6} \Delta t^3 + O(\Delta t^4)
\]  

(1.5)

\[
R(t-\Delta t) = R(t) - R'(t)\Delta t + \frac{R''(t)}{2} \Delta t^2 - \frac{R'''(t)}{6} \Delta t^3 + O(\Delta t^4)
\]  

(1.6)

The position of an atom is updated using equation by adding two equations
together:

\[
R(t+\Delta t) = 2R(t) - R(t-\Delta t) + R''(t)\Delta t^2
\]  

(1.7)
The velocity of an atom is updated using equation by subtracting two equations together:

\[
v(t) = \frac{R(t + \Delta t) - R(t - \Delta t)}{2\Delta t} = R'(t) + O(\Delta t^2)
\] (1.8)

Step 4: further simulation and computation of properties. The system will be placed into designated conditions to calculate the properties of interest. In the case of a deformation simulation, the simulation box of the system will be changed during the simulation process to match the strain rate required. The virial stress is calculated based on the discussion by Diao et al. [52]:

\[
\Pi^{\alpha\beta} = \frac{1}{\Omega} \left\{ - \sum_i m_i v_i^\alpha v_i^\beta + \frac{1}{2} \sum_{i<j} \sum_{\alpha<\beta} F_{ij}^{\alpha\beta} r_{ij} \right\}
\] (1.9)

where \(\Omega\) is the volume of the system, \(m_i\) and \(v_i\) are the mass and velocity of atom \(i\) respectively, \(F_{ij}\) is the force between particle \(i\) and \(j\), \(r_{ij}\) is the distance between atom \(i\) and \(j\). The simulated stress-strain curve can thus be obtained and analyzed for the yield stress or flow strength.

Nose-Hoover thermostat [53, 54] is a common and efficient algorithm used in classical molecular dynamics to simulate the canonical ensemble at a constant temperature. Application of the algorithm in can generate positions and velocities of micro-canonical ensemble (NVE), canonical ensemble (NVT), isothermal-isobaric ensemble (NPT), isenthalpic ensemble (NPH), where \(N\) represents a constant number of atoms, \(V\) is volume, \(E\) is energy and \(H\) is enthalpy.

In plastic deformation simulations, researchers are usually more interested in maintaining constant temperature or pressure instead of constant energy or volume.
Berendsen-thermostat is developed to reach this goal [55] by weakly coupling the system to an external bath with constant temperature or pressure. The temperature or pressure oscillation decays exponentials under Berendsen thermostat. This method will create a different ensemble from a canonical ensemble. But at large systems of hundreds or thousands of atoms, the difference is negligible.

1.4.2. Hybrid Monte-Carlo / Molecular Dynamics Simulation

A large-scale hybrid Monte-Carlo / molecular dynamics algorithm is developed to study segregation or precipitation effect [56]. Classical Monte Carlo (MC) algorithm uses random sampling to obtain numerical results. It is based on canonical ensemble [57] and difficult to study large systems due to the lack of efficient parallelization. Furthermore, semi-grand-canonical (SGC) ensemble is not suitable for studying precipitation or segregation problems because of concentration inside the miscible gap is unable to stabilize. The SGC ensemble is thus modified by adding an extra constraint named ensemble averaged squared concentration. It limits the concentration fluctuation inside the miscibility gap. The ensemble is named variance-controlled-semi-grand-canonical (VC-SGC) ensemble. The MC algorithm is applied into VC-SGC ensemble (VC-SGC-MC method) with the following steps: (1) select an atom randomly. (2) change the type of the atom. (3) calculate the change in energy and accept the trial move with a probability function as in Equation (1.10).

\[
A_{v} = \min(1, \exp\{-\beta[\Delta U + N\Delta \phi \phi + 2\kappa N\bar{c}]\})
\]  

\[\text{(1.10)}\]
where, $\beta$ is $1/k_B T$, $\Delta U$ is energy difference between two configurations, $N$ is the number of particles, $\Delta c$ is concentration difference, $\phi$ and $\kappa$ are Lagrange multiplier constraints for first and second moments of the concentration, $\tilde{c}$ is ensemble averaged concentration to limit the concentration fluctuation inside miscibility gap. The VC-SGC-MC method is further combined with MD by alternating between MC steps and MD steps during simulation, to consider chemical mixing, structural relaxation, and thermal vibrations at the same time. It is named hybrid Monte-Carlo / molecular dynamics (MC/MD) method. It allows the study of segregation or precipitation in systems with several million atoms using current computing powers. One thing worth noting that, in Sadigh’s work, two different potentials [58, 59] for Fe-Cu system are demonstrated for MC/MD simulations. The distribution of Cu atoms is highly dependent on the potential chosen. LF potential will result in a random solute distribution inside GB. PM potential will result in a precipitation of solute atoms inside GB.

Figure 1. 15: Distribution of solute Cu atoms in BCC Fe after MC/MD simulations using LF potential for (a) and (b) ; PM potential for (c) and (d). Fe, Cu, and GB atom using CNA are colored in white, blue and pink respectively in (a) and (d). GB atoms of Fe and Cu are colored in grey and blue respectively adapted from [56].
1.4.3 LAMMPS and OVITO Software

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is a widely used molecular dynamics open-sourced software from Sandia National Laboratories [60] focused on materials modeling. It runs both on a single processor and in parallel using Message Passing Interface (MPI). Molecular dynamics or Monte-Carlo simulations generate a large amount of 3D atomistic dataset for position, trajectories and other physical properties.

Open Visualization Tool (OVITO) is a tool used for further analysis and graphical insight [61]. The idea of data processing pipeline in OVITO allows complicated processes to be easily applied in a sequence. Each process adds a modification to atomistic data and the processed data can be passed on to the next process. Finally, the data can be rendered on the screen or output to a picture. Three main analyzing methods in OVITO are used in this thesis study. Common Neighbor Analysis (CNA) [62] is applied to identify four types of local structures: face-centered cubic (FCC), hexagonal close-packed (HCP), body-centered cubic (BCC) and icosahedral (ICO). Dislocations, GBs, TBs and other types of defects can be identified.

Atomic strain analysis [63, 64] can be applied to atomic data of one system at two different configurations to compute the atomic level strain tensor. CNA method can only be used to identify the microstructure of a specific system configuration. Atomic strain analysis can provide a complementary insight into how atoms in GB, TB or defects responds to the loading during deformation. Fundamental mechanisms, for example, dislocation nucleation, GB sliding and GB rotation can be observable with
atomic strain analysis. Furthermore, dislocation analysis [65] uses the surrounding atoms to detect the Burgers’ vector of a dislocation and identify dislocation types. The different dislocations can be output as line representation and quantified. For example, in an FCC system, five types of dislocations can be identified in OVITO, Shockley partial dislocation with Burgers vector 1/6<112>, perfect dislocation with Burgers vector 1/2<110>, stair-rod dislocation with Burgers vector 1/6<110>, Hirth dislocation with Burgers vector 1/3<100>, Frank dislocation with Burgers vector 1/3<111>.

1.5. Plan of the Dissertation

Chapter 2 presents the study of Cu segregation on intrinsically defective TBs. In Chapter 3, TB size effect and Cu microalloying effect on the strength and Hall-Petch behavior are presented. In Chapter 4, results on grain size effect, strongest size, and Cu heavy-alloying to retain the Hall-Petch relation are presented and discussed. The main conclusions and future research outlook of the dissertation are presented in Chapter 5. Appendices are used to provide details about supporting information from collaborators using experiments, ab initio calculations, and continuum theory.
CHAPTER 2. SEGREGATION-AFFECTED YIELDING AND STABILITY IN NANOTWINNED SILVER BY MICROALLOYING

This Chapter contains the following publication:

2.1. Abstract

Small-scale mechanics of solute atom segregation and incipient plasticity in nanotwinned Ag containing trace concentrations of Cu were studied by using large-scale hybrid Monte-Carlo and molecular dynamics simulations. It is found that solute Cu atoms are segregated concurrently to grain boundaries and intrinsic kink-like twin boundary defects during thermal annealing. Low Cu dopant contents below 1 at. % are predicted to substantially increase twin stability in nanotwinned Ag, accompanied with a pronounced rise in yield strength at 300 K. Incipient plasticity is associated with kink-step migration, grain-boundary sliding, and dislocation nucleation from grain boundaries and twin-boundary defects, which are affected by doping. Cu-dependent yield strengthening in doped nanotwinned Ag is shown to correlate with the critical stress required to initiate crystal slip emitted from grain boundaries and twin-boundary defects. These findings provide fundamental insight into the roles of twin-boundary imperfections on plastic yielding, and offer new clues to further extend the extraordinary stability and strength of nanotwinned metals by microalloying.

**Keywords:** Nanotwinned silver, atom segregation, strength, plasticity; atomistic simulation
2.2. Introduction

Nanotwinned (nt) metals are comprised of coherent twin boundaries (TBs) with nanometer-scale spacing, formed during film growth, plastic deformation or thermal annealing [1]. Nt-Cu metals have shown tensile strengths up to 10 times higher than that of conventional coarse-grained Cu [2], combined with lower electrical resistivity [3,4], higher structure stability [5], and higher corrosion resistance [6] than nanocrystalline (nc) and ultrafine-grained Cu. It is well accepted, both experimentally and theoretically, that the underpinning for strengthening in nt metals is the resistance of coherent TBs to lattice dislocation motion [7-10]. Also, recent evidence from experiments and atomistic simulations [11-13] have shown that TB defects in nt-Cu, such as nanoscale kink-like incoherent steps [14], play important roles on plastic deformation processes during dislocation-TB interactions and ductility. To date, however, it remains challenging to fundamentally understand and control how intrinsic TB imperfections contribute to plastic yielding in nt metals.

Microalloying by segregation of solute atoms to grain boundaries (GBs) has been studied extensively as an effective route for increasing both stability and yield strength in nc metallic alloys where conventional solid solution strengthening is generally absent [15-21]. The core principle is to diffuse low concentrations of solute atoms to crystalline interfaces by thermal annealing in order to either reduce the excess free energy (or volume) of the GB network [16,22] or form fine pinning precipitates inside GBs to resist grain growth [23]. Spectacular strengthening effects by GB
microalloying have been achieved successfully in nanograined face-centered cubic binary alloys with high segregation enthalpies, such as Nb-doped Cu [17,24], Ti-doped Ni [25], and Mg-doped Al [21]. In nc-Cu materials, Ozerinc et al. [24] have experimentally reported a 120% increase in nanoindentation hardness with segregated solute Nb up to 10 at.%. At 1 at.% dilute atoms and above, however, it was shown that GBs thicken into zones leading to phase separation and large elemental (Nb)-based precipitation [23], which was observed to adversely increase the electrical resistivity [26]. Similarly, Zhang et al. [19] have observed that segregating Zr atoms to 0.5 at.% increased hardness, ductility and fatigue resistance in nc-Cu, but GB strength weakening was observed above 2 at.% Zr due to amorphous phase formation. Furthermore, different atomistic simulation studies in Ag-doped Cu alloys with sub-15nm grain diameters [17,27] predicted that tensile yield strength increased linearly by 30% with Ag microalloying up to 1.5 at.%, before decreasing at high concentrations, due to Ag doping effects on GB free volume. One study [27], however, suggested that the strengthening efficiency by GB microalloying with Ag atoms was reduced at a larger grain size, i.e. 40 nm.

Despite rapid progress in nc metals, the influence of microalloying on strength and stability in nt metals remains largely unexplored. In this study, large-scale hybrid Monte-Carlo and molecular dynamics (MC/MD) simulations were performed to study atomic-scale segregation processes from microalloying in nt-Ag containing trace concentrations of Cu up to 0.8 at. %, and understand their roles on incipient yielding mechanisms. Experimentally, sputter-deposited Ag films are well known to form
abundant nanotwins due to the low stacking-fault energy of this metal [28-30]. Our simulated nt-Ag samples were made of a relatively large grain size (45 nm) holding a high density of kinked or perfect nanotwins, like in those experiments. Remarkably, we find that Cu dopant is strongly segregated to TB kink defects during annealing, in addition to traditional GB doping, which dramatically enhances twin stability under high stress. Microalloying gives rise to nearly two-fold increase in yield stresses with low elemental amounts of Cu (< 1 at. %). The objective of this study is to determine the atomic mechanism(s) governing the dependence of yield strength on Cu dopant concentration.

2.3. Computational Methods

Hybrid MC/MD simulations [22,31] were performed to structurally and chemically relax large-scale and small-scale nt-Ag models containing Cu dopant concentrations between 0% and 0.8 at. %. The software LAMMPS [32] was used with an embedded-atom method (EAM) potential for Ag-Cu binary alloys by Wu and Trinkle [33]. This potential was fitted from ab-initio data to match surface atom diffusivities and generalized stacking-fault energy curves in this system. Our own simulations with this potential showed that the unstable and stable stacking-fault energies in pure Ag were equal to 115.3 mJ/m² and 16.6 mJ/m², respectively. We found that the generalized stacking-fault energy curve remained unchanged by randomly adding Cu atoms up to 5 at. % concentration, which indicated that solid solution
strengthening was absent. Large atomistic models of dimensions 90 nm × 90 nm × 90 nm were created in Ag with a total of 42.6 million atoms, as shown in Figure 2.1(a).

Figure 2. 1: Atomistic models used for simulations of solute atom segregation and tensile deformation in (a) nanotwinned (nt) Ag with kinked TBs of 2.8 nm in thickness and an average grain size of 45 nm, and (b) nt-Ag bicrystal containing only one single TB kink defect. (c) Atomic structure in a TB kink step. Atoms in perfect fcc arrangement are colored in blue, coherent TBs in red color, GB and TB defects in yellow color.

Seven grain regions of 45 nm in average diameter were created by Voronoi tessellation scheme with randomly distributed grain centers, random crystallographic orientations, and fully periodic boundary conditions, similar to our previous work [34]. GB atoms closer than 0.5 Å were removed. Each grain contained constantly spaced TBs created by mirror-copying operation on the FCC stacking sequence along the [111] direction. A small TB spacing of 2.8 nm was used, because the effect of microalloying on twin stability was expected to be more prominent with a smaller TB spacing and this spacing is more vulnerable to detwinning through partial dislocation glide [8]. Two types of model comprised of either kinked or perfect TBs were considered. Small-scale
atomistic models consisted of a GB-free nt-Ag bicrystal containing one single TB kink, as shown in Figure 2.1(b). Bicrystal models were 24 nm × 4 nm × 14 nm with periodic boundary conditions and 83,000 atoms. The atomic structure of each kink step was equivalent to repeating pattern \( b_2 : b_1 : b_3 \) of an incoherent \( \Sigma 3[112] \) TB, with Burgers vectors \( b_1 = 1/6[\overline{1}12] \), \( b_2 = 1/6[1\overline{2}1] \) and \( b_3 = 1/6[2\overline{1}1] \), characterized by a zero sum [35]. The minimal energy configuration of a kink-step defect reached by conjugate gradient method is shown in Figure 2.1(c). Before MC/MD simulation, the steps in large scale models were uniformly distributed with a separation distance of 10 nm, following past observations made by transmission electron microscopy [11]. The step height was 0.7 nm.

The energy of each model was minimized by conjugate gradient method. The structure was then relaxed under zero pressure using an isothermal–isobaric (NPT) ensemble at 450 K for 100 ps, then cooled to 300 K in 50 ps, and held at the same temperature for another 50 ps. Temperature was rescaled every 500 steps. The timestep was 5 fs, which was found to conserve the total system energy. The hybrid MC/MD approach used to simulate Cu atom segregation followed the method presented in [36]. Our goal was to simulate a thermal annealing process of relevance to past experiments in nt-Ag prepared using magnetron sputtering technique [1]. In particular, vacuum annealing at a minimum temperature of 423 K was applied after sputtered deposition by Bufford et al. [37] to study the thermal stability of twins in nt-Ag. Therefore, our simulations were run at 500 K for 1 million MD steps with a timestep of 2 fs and calls to MC every 10 MD steps. Temperature of MD was controlled by rescaling every 10
steps and pressure was maintained to 0 bar using a Berendsen barostat. The MC simulation part was carried out with a chemical potential difference $\Delta \mu = -2.5$ eV, variance of Lagrange multiplier $\kappa = 100$ and target Cu concentrations of 0.2, 0.4, 0.6 and 0.8 (in at.%). The simulation output showed that standard deviation of Cu at. % was about $1.0 \times 10^{-5}$ and the acceptance ratio was close to $2.5 \times 10^{-6}$. After segregation, the models were relaxed again in NPT ensemble under zero pressure from 500 K to 300 K for 100 ps, and kept at 300 K for another 100 ps.

The large-scale models were deformed in pure tension by stretching the simulation boxes at an engineering strain rate of $10^8$ s$^{-1}$ along the x direction until 3% strain. NPT ensemble at 300 K and zero pressure applied laterally along the z and y directions was used. Bicrystal models were subjected to three different loading modes corresponding to shearing up to 10% strain on either xy, xz or yz planes, respectively. The average tensile or shear stresses were computed by adding the corresponding Virial-theorem stress component over all atoms, and dividing by the deformed volume of the simulation box. The 0.2% offset yield stress was determined by fitting the linear portion of the stress-strain curves up to the stress at which the first dislocations or GB plasticity were detected. Plastic deformation mechanisms were studied by common neighbor analysis (CNA) and atomic strain analysis in the software OVITO [38]. A network of three-dimensional cells of ~1 nm in wall thickness encompassing each GB interface in the model was created by Voronoi tessellation method [39] to identify a list of GB atoms before deformation. We did not use CNA for GB atom detection, to avoid adding extra atoms from kink defects present inside the grains. The average atomic
shear strain was calculated in the estimated GB network as a function of applied strain. The onset of GB plasticity was defined as the configuration reaching an average shear strain in GBs of 0.05, which was determined from detailed analysis of atomistic simulation snapshots at different strains. The simulations were performed on the high-performance SuperMIC supercomputer in the Extreme Science and Engineering Discovery Environment (XSEDE) [40].

2.4. Results

2.4.1 Equilibrium Cu Segregation in Nanotwinned Ag

Equilibrium Cu atom distributions with Ag atoms deleted, as obtained after hybrid MC/MD simulations at a concentration of 0.8 at. % Cu, are shown in Figures 2.2 (a) and 2.2 (b) for large-scale nt-Ag models with kinked and perfect TBs, respectively.
Figure 2. Hybrid MC/MD simulations of segregation of 0.8 at. % Cu atoms in nanotwinned Ag during 500 K annealing. Equilibrium Cu atom distribution simulated in large-scale nt-Ag model containing (a) kinked TBs and (b) perfect TBs. (c) Close-up view on Cu segregation to GB and TB kink steps in (a). (d) Average local Cu concentration inside GB region in (a) and (b). (e) Cu atom distribution (0.8 at.%) after segregation in GB-free bicrystal model containing one kink defect. Cu atoms segregated to TB kink steps and GBs are colored in yellow, those moved to coherent TB segments in red, and other atoms staying in solution are in blue color. The position of individual TB kink steps was indicated with a red arrow.
In the model with perfect TBs, it is found in Figure 2.2 (b) that after thermal annealing, large majority of Cu atoms are segregated to the GBs, with less Cu atoms in the grain interior. Dopant atoms left inside grains are randomly distributed at both face-centered cubic and hexagonal close-packed lattice sites, suggesting perfect alloying element dilution. By contrast, the model with kinked TBs in Figure 2.2 (a) shows evidence that a significant fraction of dopants is attracted by intrinsic TB kink steps to form extended lines of Cu atoms inside the grains, alongside GB segregation.

A close-up view of a thin slice in Figure 2.2 (c) reveals that Cu atoms were not segregated to the coherent TB segments, but more preferentially to TB steps and GBs. Qualitatively, it appeared as if Cu doping was equal in both types of defect. Quantitatively, in Figure 2.2 (d), we estimated the local Cu concentration segregated in the three-dimensional GB network. Here the local dopant concentration in GB was calculated using the ratio of Cu atoms over total number of Ag and Cu atoms in the GB network. Different values of half GB wall thickness $x$, as schematically shown in inset of Figure 2.2 (d), were chosen from 0.24 nm to 1.4 nm by considering $x$ as multiples of the (111) interplanar distance in Ag. With perfect TBs and 0.8 at.% Cu concentration, the local Cu concentration near the GB center reached 11.5 at.% suggesting that, even in small amount, Cu dopants are strongly attracted by sites in the GB core. Interestingly, in the presence of TB defects such as kinks, Figure 2.2 (d) also reveals that the highest local Cu concentration in GB decreased to 10 at.%, indicating that atom segregation to TB kink steps inside the grain has become significant. We verified this
hypothesis by simulating the process of Cu atom segregation in the GB-free bicrystal model, Figure 2.1 (b), with an equivalent dopant concentration of 0.8 at.% Cu. Figure 2 (e) shows that most substitutional sites along the two TB kink steps are replaced by Cu atoms, and that the reminder of dopants stays randomly distributed in solution. No preferential segregation to coherent TB segments is found.

2.4.2 Incipient Plasticity Mechanisms

To understand the effects of Cu dopant segregation on stability and yielding of doped nt-Ag, plasticity mechanisms around the yield point at 300 K were studied for different segregated Cu contents. First, incipient plastic deformation processes in a representative nt-Ag grain from the large-scale model containing perfect TBs are presented in Figure 2.3 [41].

Figure 2. 3: Incipient plastic deformation mechanisms at 300 K in undoped and Cu-doped nanotwinned Ag containing perfect TBs. (a) Atomistic snapshots of microstructure in nt-Ag before
deformation. Atoms in perfect fcc arrangement have been omitted for clarity. (d) Stress-strain curves at yielding with different Cu contents. Deformed microstructures and corresponding atomic von-Mises shear strain (\(\varepsilon_{vm}\)) distributions in undoped nt-Ag at (b), (e) 1.5% strain and (c), (f) 2.5% strain.

GBs are found to be stable with limited migration during deformation up to 3% strain. In undoped nt-Ag, the onset of plastic deformation is characterized by GB plasticity in the form of interface sliding, Figure 2.3 (b) and 2.3 (e), followed by nucleation of extended partial dislocation loops from GBs, Figure 2.3 (c) and 2.3 (f). They clearly show that all dislocation loops are emitted from GBs and propagate on (111) slip planes parallel to TBs. This result mostly agrees with the atomistic simulation study by Li et al. [8] in nt-Cu at small TB spacings, at the exception that dislocation emission is distributed along GBs and not site-specific in nt-Ag, while it was always localized at GB-TB triple junctions in nt-Cu.

With Cu dopant addition, Figure 2.4 (f) [41] shows significant improvement in microstructure stability up to 3% strain. Stress-strain curves shown in Figure 2.3 (d) indicate that the onset of GB plasticity always occurs before dislocation nucleation. It is observed, however, that the critical stresses at onsets of GB plasticity and dislocation nucleation increased substantially with Cu content, and that the stress difference between these two events is reduced 10-fold as Cu content increases. Specifically, in nt-Ag doped with 0.8 at.% Cu, dislocation nucleation is rapidly initiated after the stress is augmented by 60 MPa above that for the first GB sliding event, in contrast to 600 MPa in its undoped equivalent.
Now, we shift attention to the stability and yielding of nt-Ag containing TB kink imperfections, as shown in Figure 2.4 (a) before deformation.

![Image of atomistic snapshots of microstructure in nt-Ag before deformation.](image)

**Figure 2.4:** Incipient plastic deformation mechanisms at 300 K in undoped and Cu-doped nanotwinned Ag containing imperfect kinked TBs. (a) Atomistic snapshots of microstructure in nt-Ag before deformation. Atoms in perfect fcc arrangement have been omitted for clarity. (d) Stress-strain curves at yielding with different Cu contents. Deformed microstructures and corresponding atomic von-Mises shear strain ($\varepsilon_{vm}$) distributions in undoped nt-Ag at (b), (e) 1.5% strain and (c), (f) 2.5% strain. M = Detwinning by TB kink migration and S = Dislocation nucleation by TB kink splitting.

Two atomistic simulation snapshots of the same grain deformed at 2.5% tensile strain in undoped and doped nt-Ag are compared in Figure 2.4 (b) and 2.4 (c), respectively. In Figures 2.4 (b), 2.4 (e) [41] depicting the behavior of pure nt-Ag, majority of kink steps are shown to migrate easily along TBs under stress. Migrating kink steps are either merged with neighboring ones with opposite Burgers vectors or absorbed into a nearby GB to produce perfectly coherent TB segments. Therefore, it is possible to regard kink migration as a lower limit of twin instability, since this process
leads to detwinning. In Figure 2.4 (b), several kink steps can be observed to dissociate into partial dislocations gliding independently along the supporting TB. This process involves the emission of one or two twin partial dislocations splitting from the initial \( b_1:b_2:b_3 \) kink step structure presented in Figure 2.1 (c). It is worth noting that kink migration is somewhat different from kink splitting, because the former involves motion of three \( b_1:b_2:b_3 \) partial dislocations altogether [13].

In the case of Cu-segregated nt-Ag models, Figures 2.4 (c) and 2.4 (f) show that kink migration and splitting were both simulated, but the latter mechanism was significantly more dominant, as only a few kinks very close to GBs could be found to migrate and be absorbed under stress. It should be pointed out that in splitting, kink steps have been converted into new dislocation nucleation sites, consistent with recent experimental observations made in nt-Cu metals [12]. Therefore, these results show that the primary Cu segregation effect on plastic deformation mechanisms is to reduce twin instability by shifting from kink-step migration in pure nt-Ag to kink-mediated dislocation nucleation in doped nt-Ag, which is also confirmed by the bicrystal simulations below.

The dependence of yielding mechanisms on stress and Cu content in defective nt-Ag is summarized in Figure 2.4 (d). Incipient plasticity in this type of metal relates to kink-step migration, grain-boundary sliding, and dislocation nucleation from GBs and TB defects, which are affected by Cu dopant concentration. Importantly, Figure 2.4 (d) shows that kink migration takes place at much smaller stress than the onsets of GB plasticity and dislocation nucleation, at any Cu contents. Like nt-Ag with perfect TBs,
however, the stress difference between plasticity events decreases dramatically with increasing Cu amounts, which provides evidence that microalloying has enhanced twin stability and yield strength in unison.

2.4.3 Dependence of Yield Strength on Cu Segregation

Critical stresses at the onsets of TB kink migration, GB sliding and dislocation nucleation as functions of segregated Cu content, are presented in Figures 2.5 (a) and 2.5 (b) for perfect and kinked TBs, respectively. 0.2% offset yield stresses determined from the stress-strain curves presented in Figures 2.3 (d) and 2.4 (d) have been included for comparison. At the same Cu content, we find that offset yield stresses in doped nt-Ag are smaller with kinked TBs than with perfect ones.
Figure 2.5: Dependence of yield strength on Cu doping in nt-Ag containing (a) perfect TBs and (b) kinked TBs.

Yield strength relates to Cu concentration almost linearly. From 0% to 0.8 at.% Cu doping, yield stress in nt-Ag increases from 1.26 GPa to 2.13 GPa (69% rise) in the presence of perfect TBs, and from 1.09 GPa to 2.00 GPa (83% rise) with kinked ones. In addition, Figure 2.5 confirms that Cu segregation affects the critical stress to activate each mechanism. Yet, the Cu dependence of offset yield strengths is found to match
more closely the Cu dependence for the onset of dislocation nucleation for both perfect and imperfect TBs.

To further investigate the fundamental roles played by Cu segregation on the stability and yielding of intrinsic TB kink steps alone, plastic deformation mechanisms in GB-free bicrystals subjected to pure shear loading are presented in Figure 2.6. Figures 2.6(a)-(c) show that undoped bicrystals are predominantly deformed by kink annihilation through step migration at approximately same stress under all shear loading conditions.

Figure 2. 6: Intrinsic Cu segregation effects on plastic yielding of a twin-boundary kink defect in GB-free kinked bicrystals subjected to pure shear loading on different planes. (a)-(c) Yielding...
mechanisms with and without Cu doping for shearing in either xy, xz or yz shear planes. (d) Critical yield stress as a function of segregated Cu content.

However, Figure 2.6 (d) suggests pronounced Cu segregation strengthening up to 0.75 at.% Cu, followed by a plateau at constant strength for higher dopant concentrations. Simultaneously, the yielding mechanism of TB kink steps is found to change from defect migration to nucleation of lattice dislocations in the form of either in-plane kink splitting or inclined 60° dislocation, as indicated by S and N symbols, respectively.

2.5. Discussion

A major finding of this study is that both twin stability and yield strength in nt-Ag metals are proven to increase substantially by introducing trace concentrations of Cu solute atoms. A striking feature discovered in our simulations is the importance of dilute Cu atoms segregating towards intrinsic TB kink-step defects, together with classical GB segregation. Periodic segregation of rare-earth Gd solute atoms at fully coherent TBs has been observed in a recent experimental study in hexagonal-close packed Mg alloys [42]. These TBs were formed by deformation twinning, and solute atom segregation acted to relieve the residual elastic strain caused by local compression sites. On the contrary, coherent TB segments in the present nt-Ag models were fully relaxed and strain-free, and thus their role was found to be inconsequential for
equilibrium Cu segregation. Therefore, solute atom segregation to TB defects in nt-Ag can be viewed as significant in several aspects.

First, it demonstrates that Cu segregation by microalloying can directly impact on twin stability in nt-Ag in the absence of solid solution strengthening. TB kink steps are made of three dislocations whose Burgers vector sum is null. So, this type of defect can easily glide in full along TBs at low applied shear stress, giving rise to permanent detwinning by step annihilation or absorption at GBs, as shown in Figures 2.4 (d) [41]. The present study shows that the pinning of TB kink steps due to atom segregation is central to twin stability. Apparently, similar atomic processes were recently observed in α-Fe where dislocations were found to be strongly pinned by substitutional He segregation [43]. As shown in Figure 2.6, with less than 1 at.% Cu concentration, the critical shear stress to plastically deform a kink defect in a bicrystal can be increased by a factor between 33% and 200%, depending on the loading direction. In large-scale polycrystal models, the tensile stress at twin instability was remarkably increased by more than 300% at 0.8 at.% Cu. In pure nt-Ag metals synthesized experimentally, the smallest TB spacing reported so far has been ~8 nm [28-30]. The above theoretical predictions, however, suggest that even smaller TB spacings could possibly be achieved in this metal by microalloying.

Second, low Cu concentrations (≤ 0.8 at.%) were found to efficiently increase the overall yield strength by 83% from that of undoped models with identical microstructures. This result is significant with respect to previous studies on GB strengthening effects from dilute atom segregation in the Cu-Ag alloy system. Vo et al.
[17], using the same simulation approach than here, described that the yield strength of nc-Cu increased by only 15% by GB doping with 0.8 at.% Ag. Also, with similar local concentrations in GBs, Li and Szlufarska [27] simulated that the 0.2% offset yield stress increased by 23% in nc-Cu by Ag doping, with a grain size of 40 nm, close to that examined in the present models. This comparison therefore implies that GB strengthening alone cannot entirely account for the exceptional strengthening observed in the present study, and that other Cu-dependent strengthening mechanisms could be at play.

Third, offset yield stresses in large-scale nt-Ag polycrystals with different Cu concentrations were found to closely match the segregated Cu dependence of critical stress to initiate crystal slip in nt-Ag models with both perfect and imperfect TBs. This observation provides numerical evidence that dislocation emission is the dominant yielding mechanism in this material. We find GB sliding to be a precursor for dislocation nucleation, which is in agreement with past atomistic simulations of incipient plasticity in nc metals [34]. The same mechanism is predicted to hold with Cu doping, albeit the stress difference at the onsets of GB sliding and crystal slip is dramatically reduced with increasing dopant concentration. This can be attributed to the role of atom segregation in decreasing the excess free volume at GBs. This phenomenon was studied in nc Ni-Fe and Cu-Ag alloys [18,27] where a direct relationship between segregation affected excess GB free volume and offset yield stress was proposed. The finding that GB-mediated dislocation nucleation is distributed and not site-specific tends to support this hypothesis. Another interesting result obtained
here is that TB kink steps become primary nucleation sites for crystal slip at yielding, in addition to GB-mediated dislocation nucleation. As such, this study presents a new type of yield stress dependence on atom segregation based on Cu affected dislocation emission from TB defects.

2.6. Conclusion

Hybrid MC/MD simulations have been used to study the atomic processes of Cu segregation in microalloyed nt-Ag metals. A major conclusion is that both twin stability and yield strength in nt-Ag metals are increased substantially by introducing trace concentrations of Cu solute atoms less than 1 at.%. Preferential segregation of Cu atoms towards intrinsic TB kink steps was found to promote twin stability and resistance to detwinning by pinning of TB defects, alongside classical GB segregation. In addition to GB strengthening, doping is found to fundamentally change the plastic deformation of TB defects from migration to kink-activated crystal slip. It was shown that yield strength is directly associated with the Cu-dependent critical stress for dislocation nucleation at GBs and TB defects. This study suggests that microalloying may enable the design of new nt metals with superior strengths and structure stability that could potentially exceed the current limits.

2.7. Acknowledgements
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2.8. References

See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.1.063604 for movies of MD simulation of plastic yielding up to 3% applied strain in undoped nt-Ag containing perfect coherent TBs (movie S1), undoped nt-Ag containing imperfect kinked TBs (movie S2), and doped nt-Ag with 0.8 at. % Cu containing imperfect kinked TBs (movie S3). The time interval between two snapshots is 5 ps.


CHAPTER 3. IDEAL MAXIMUM STRENGTHS AND DEFECT-INDUCED SOFTENING IN NANOCRYSTALLINE-NANOTWINNED METALS

The content of this work has been adapted and split into 2 parts for presenting in this thesis:

1. Molecular dynamics simulation study from author of this thesis is presented in this chapter.

2. Collaborators’ works are presented in Appendices.
3.1 Abstract

Experiments and simulations have demonstrated that strengthening metals through nanoscale grain boundaries and coherent twin boundaries is manifested by a maximum strength—a phenomenon that is known as Hall-Petch breakdown. The softening mechanisms have been considered drastically different between nanocrystalline and nanotwinned materials. Here we report that nanocrystalline-nanotwinned Ag materials exhibit two strength transitions that are fundamentally dissimilar from the formerly known mechanisms. Atomistic simulations show three distinct strength regions as the twin spacing decreases, delineated by positive Hall-Petch strengthening to grain-boundary-dictated (near-zero Hall-Petch slope) defects. For materials with perfect twin boundaries, unexpectedly, a maximum strength is reached without any sign of softening. This work demonstrates the potential for creating interface-dominated materials with unprecedented mechanical and physical properties.
3.2 Introduction

Although the mechanisms underpinning Hall-Petch (HP) hardening and softening in nanocrystalline (nc) and nanotwinned (nt) materials have been investigated for several decades [1-9], an interesting scenario may arise when a metal is strengthened by both grain boundaries (GBs) and twin boundaries (TBs); i.e., in a new class of nc and nt materials (we term them as nnt-materials from here on). The existing theories suggest drastically different breakdown mechanisms in these two types of materials; i.e., the former is caused by grain-boundary sliding [3] and the latter by dislocation-nucleation governed plasticity [6]. To date, the atomic softening mechanisms have been garnered by molecular dynamics (MD) simulations of materials containing nanosized grains (≤70 nm) [2, 3, 6]. It has been a longstanding challenge to experimentally verify or disapprove these mechanisms due to the technological difficulty of synthesizing nanostructured materials with microstructures that are as ideal and infinitesimal as those used in these models. For pure nt metals, the grain sizes (d) of as-synthesized materials are larger than 100 nm [5, 10, 11], precluding experimental investigations of the truly nc region. It thus remains scientifically significant to experimentally interrogate the strength behavior in nt materials with d well below 100 nm, where GBs and TBs could become competing strengthening mechanisms.

We choose silver (Ag) as a model material system to investigate the HP strengthening and softening in nnt-materials. Ag is a low stacking fault metal (~16 mJ·m⁻²) [12] and known to form copious growth nanotwins during magnetron sputtering processes [13, 14]. However, the smallest d achieved using this method is
~150 nm [14]; i.e., outside the nc region. Heavily alloying is a common strategy to reducing d but inevitably complicates the fundamental mechanism studies due to the hardening effects of solutes [15], or a change of stacking fault energies in Ag caused by alloying that alters root deformation mechanisms. For above reasons, we developed a microalloying (or doping) strategy by carefully selecting Cu as the primary impurity—a solute that is predicted by our own simulations to have no solid-solution strengthening effect in Ag when its content is below 3.0 wt.% as shown in Figure 3.1.

Figure 3. 1: Investigations of Cu solute strengthening in Ag metals by MD simulation. (a) Tensile deformation of a nt-Ag polycrystal model with a small grain diameter of 20 nm and large TB kink-steps of 1.4 nm in height, as shown in inset. (b) GB segregation of 1.8 wt.% Cu atoms by hybrid MC/MD simulation. Such a relatively high concentration is four times larger than that in our atomistic model with a 45-nm grain size presented in Figure 3.2. GB segregation strengthening is evident in the stress-strain curve in (a). (c) Random Cu distribution to reproduce a state of perfect solid solution. The stress-strain curve in A shows no solution hardening effect with random Cu additions (without annealing and segregation) up to at least 3 wt.% Cu. (d) We computed the generalized stacking-fault energy curve, which relates to the critical energies for nucleating partial dislocations and stacking faults in Ag and also found no influence with random Cu concentrations up to 3 wt.% Cu. $\gamma_{SF}$ and $\gamma_{USF}$ are the stable and unstable stacking-fault energies, respectively. Together, these results demonstrate that solid solution strengthening was absent for the impurity concentration investigated in this study.
Neither will Cu affect the stacking fault energy of Ag at a concentration <1.0 wt.%. Moreover, Cu atoms are ~12% smaller than Ag and Ag-Cu is an immiscible system, which facilitates the segregation of Cu into high-energy interface sites such as GBs and TB defects [11]. We performed atomic simulations, applying the experimental d value and varying λ. Several new regimes of HP strengthening and softening are uncovered. Interestingly, we further discover that the softening behavior is fundamentally different between “ideal” materials with perfect TBs and “real world” materials containing TB defects.

3.3 Methodology

Large-scale MD simulations were performed using the massively parallel software LAMMPS [16] with the embedded-atom-method potential for Ag-Cu system by Wu and Trinkle [17]. This potential was fitted from ab-initio data to match surface atom diffusivities and generalized stacking-fault energy curves in this system. Our own simulations with this potential showed that the unstable and stable stacking-fault energies in pure Ag were equal to 115.3 mJ/m² and 16.6 mJ/m², respectively (Figure 3.1 (d)). The atomistic samples consisted of a cubic simulation box with periodic boundary conditions on each of the xyz spatial directions. This box was 90nm × 90nm × 90nm in dimensions and contained 42.6 million atoms. Seven grains with random crystal orientations and random centers were created by placing atoms in the simulation box using a Voronoi tessellation scheme. GB atoms closer than 0.5 Å were automatically removed at this stage. Each grain contained constantly spaced twin
boundaries perpendicular to the [111] direction. The twin spacing was varied from 1.4 nm to 21.9 nm between different models. A TB kink defect of 0.7 nm (3 atomic layers) in height in the [111] direction was introduced on each twin boundary. Each kink formed two steps perpendicular to the [ $\bar{1}12$ ] direction and separated by 10 nm, following past experimental observations [11]. The total energy of each sample was minimized at 0K by conjugate gradient method. The structure was further relaxed under zero pressure using an isothermal–isobaric (NPT) ensemble at 450 K for 100 ps, then cooled to 300 K in 50 ps, and held at the same temperature for another 50 ps. Temperature was rescaled after every 500 steps. The time step was 5 fs, which was found to conserve the total energy of the system. The samples were deformed in pure tension by stretching the simulation box at an engineering strain rate of $1 \times 10^8$ s$^{-1}$ along the x direction until 10% strain was reached after 1 ns. We used the NPT ensemble at 300 K and applied zero pressure laterally along the z and y directions. Atomic stresses from the Virial theorem and the deformed volume of the simulation box were used to compute the true stress - true strain diagrams. Atomistic snapshots were created by common neighbor analysis and atomic strain analysis in the visualization software Ovito [18]. The MD simulations were performed on SuperMIC supercomputer of the Extreme Science and Engineering Discovery Environment (XSEDE) and Cori supercomputer of the National Energy Research Scientific Computing Centre (NERSC).

A hybrid MC/MD approach [19, 20] in LAMMPS was used to simulate the segregation of Cu atoms in nnt-Ag. This method was performed in the variance-
constrained semi-grand-canonical (VC-SGC) ensemble, which simulates multicomponent alloys within the miscibility gap, with both chemical, structural, and thermal relaxations. The hybrid MC/MD simulation was run at 500 K for 1 million MD steps with a time step of 2 fs and calls to MC every 10 MD steps. Temperature in MD was controlled by rescaling every 10 steps and pressure was maintained to 0 bar using a Berendsen barostat. The MC simulation part was done with a chemical potential difference $\Delta \mu = -2.5$ eV, variance of Lagrange multiplier $\kappa = 100$ and target concentration up to 1.3 at.% (or 0.77 wt.%). The simulation output showed that standard deviation of Cu at. % was about $1.0 \cdot 10^{-5}$ and the acceptance ratio was close to $2.5 \cdot 10^{-6}$. Before deformation, each segregated model was further relaxed in NPT ensemble under zero pressure from 500 K to 300 K for 100 ps, and kept at 300 K for another 100 ps. The MC/MD simulations were performed on the XSEDE’s SuperMIC and NERSC’s Cori supercomputers.

### 3.4 Results

Large-scale hybrid Monte-Carlo (MC) and MD simulations involving a total of 2.2 billion atoms were used to study ten $\lambda$ values from 1.4 to 21.9 nm, with either kinked (i.e., defective [11]) or perfect coherent TBs. The d in our nt-Ag models is fixed at 45 nm (i.e., similar to the experiments), corresponding to a GB atom fraction of 3 %.
Figure 3.2: Hall-Petch strength transition zones in pure and impurity-segregated nanotwinned Ag metals containing either perfect or kinked twin boundaries obtained by large-scale atomistic simulations. (a-b) Snapshot of hybrid Monte-Carlo and molecular dynamics simulation of microstructure relaxation and equilibrium impurity segregation after 500 K annealing in nt-Ag with a target concentration of 0.47 wt.% Cu, $\lambda = 3.5$ nm and $d = 45$ nm. First, common neighbor analysis is performed to differentiate atoms from coherent twin boundaries (magenta color), incoherent interface defects (dark purple), and face-centered cubic (FCC) atoms (light grey). Second, Ag atoms are removed from one of the corner regions to highlight its Cu impurity distribution. In this region, Cu atoms are colored in green, dark purple and blue when found at incoherent interfaces, coherent twin-boundaries, and FCC lattice, respectively. (c) Hall-Petch flow strength plots for pure and Cu-segregated nt-Ag with either kinked TBs or perfect coherent TBs, as a function of $\lambda$.

Twin-free nc-Ag is also simulated as a comparison, since this material has never been studied before. Figure 3.2 (a) displays a simulated nt-Ag microstructure containing equally spaced nanotwins of size $\lambda = 3.5$ nm, and the equilibrium impurity distribution of 0.47 wt.% Cu atoms after 500 K annealed conditions. It indicates that most Cu atoms are preferentially segregated into GBs and TB kink-step defects, Figure 3.2 (b). Selective Cu segregation gives rise to marked strengthening effects in nt-Ag materials [21]. From our MC/MD simulations, it is evident that, by segregating a small amount of Cu atoms, GBs and TB defects are firmly pinned down during plastic deformation in Figure 3.3, while yield stresses at the initiation of GB sliding and GB-nucleated dislocations rise dramatically in Figure 3.4.
Initial microstructure

Microstrain from 5% to 7% deformation

Grain-boundary shear strain (%) vs Applied strain (%) for different TB spacings:

- $TB = 1.4$ mm
- $TB = 2.1$ mm
- $TB = 2.8$ mm
- $TB = 3.5$ mm
- $TB = 4.3$ mm
- $TB = 6.3$ mm
- $TB = 7.7$ mm
- $TB = 9.9$ mm
- $TB = 14.6$ mm
- $TB = 21.9$ mm
- No CTB

Onset of plastic yielding

GB shear strain rate vs TB spacing

GB stress at 0% strain vs TB spacing
Figure 3. 3: Transition from positive Hall-Petch strengthening to GB-stress-controlled (near-zero HP slope) mechanisms. MD snapshots of (a) and (b) initial microstructure before deformation and (c) and (d) of local von-Mises shear strain accumulated from 5% to 7% applied strains in Cu-segregated nt-Ag with $\lambda = 14.8$ and 3.5 nm, respectively. The GB-mediated plasticity by sliding increases as $\lambda$ decreases. (e) Average shear strain per GB atom as a function of applied strain. Strong dependence on $\lambda$ is only seen with the plastic flow regime, but not at yielding. (f) The average shear strain rate per GB atom increases substantially as both $\lambda$ and impurity segregation increase, but also reach a plateau below a critical twin spacing transition. (g) Average atomic tensile stress $\sigma_{xx}$ per GB atom at 5% applied strain in pure and Cu-segregated nt-Ag., showing significantly higher GB stresses with Cu-impurity segregation.

Figure 3. 4: Influence of Cu impurity concentration on mechanical behavior in nanocrystalline-nanotwinned Ag and twin-free nanocrystalline Ag. (a) and (b) Stress-strain curves in nnt-Ag ($d = 45$ nm, perfect TBs, $\lambda = 2.8$ nm) and nc-Ag ($d = 45$ nm, no TB). (c) Plastic flow strength for the two materials is characterized by segregation strengthening and a maximum strength limit achieved with small Cu concentrations.

Dislocation nucleation mechanisms occur at higher stresses, because solute segregation to GBs significantly reduces the excess GB free volume [22, 23] (Figure 3.5).
Steady plastic flow is established by applying more than 4% strain. In this state, the average flow strength increases with impurity addition, with a maximum reached at only 0.12 and 0.47 wt.% Cu in twin-free nc-Ag and nt-Ag materials, respectively (Figure 3.4 (c)). The impurity-dictated strengthening is well beyond the hardening normally expected from solid solution strengthening based upon Fleischer model or solute pinning model proposed for heavily alloyed nc metals [24, 25].

3.5 Discussion
Our atomistic simulations suggest that solid solution strengthening is totally absent in this material with random Cu distributions up to 3.0 wt.% (Figure 3.1).

Above simulation results demonstrate that selective impurity segregation provides a means for probing the HP limit and associated softening mechanisms currently unknown in nt-Ag metals. Figure 3.2 (d) exhibits the HP plots of flow strength (i.e., the average stress from 5% to 7% applied strain) as a function of $\lambda$, simulated for pure and Cu-segregated nt-Ag metals. For the latter, the impurity concentration is fixed at 0.47 wt.% Cu. A normal HP strengthening region is observed for all $\lambda \geq 6.3$ nm, which is determined from the relationship

$$\sigma_{\text{flow}} = \sigma_0 + \frac{K_{\text{GB}}}{\sqrt{d}} + \frac{K_{\text{TB}}}{\sqrt{\lambda}}$$

where $\sigma_0$, $K_{\text{GB}}$ and $K_{\text{TB}}$ are material-dependent constants.

**Determination of Hall-Petch relation parameters**

Lu et al.[26] have proposed a generalized form of the classical HP relation applicable to the plastic flow stress of nanotwinned Cu when both the grain size $d$ and TB spacing $\lambda$ vary in Equation 3.8, where $\sigma_0$, $K_{\text{GB}}$ and $K_{\text{TB}}$ are fitting parameters. HP strengthening behavior of our nc-Ag models with $d \geq 12$ nm is associated with the formation of extended Shockley partial dislocations. This mechanism proves that the $d^{-1/2}$ scaling in Equation 3.8 relates to the density of GB dislocation sources [27], which is proportional to $1/d$ at a fixed strain for ultra-fine grained materials [23, 28].
For each material data shown in Figure 3.2 (c), we have fitted Equation 3.8 using only simulation results such as $\lambda \geq 7 \text{ nm}$ and $d = 45 \text{ nm}$. The fitting parameters obtained are given in Table 3.1.

Table 3.1: Hall-Petch equation parameters for pure nt-Ag and Cu-mixed nnt-Ag

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_0$ (GPa)</th>
<th>$K_{TB}$ (GPa$\cdot$nm$^{0.5}$)</th>
<th>$K_{GB}$ (GPa$\cdot$nm$^{0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomistic simulation results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Figure 3.2):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure nt-Ag (kinked &amp; perfect TBs)</td>
<td>0.66</td>
<td>0.80</td>
<td>3.00</td>
</tr>
<tr>
<td>Cu-segregated nt-Ag (kinked &amp; perfect TBs)</td>
<td>0.66</td>
<td>1.09</td>
<td>3.40</td>
</tr>
<tr>
<td>Experimental results by Dr. YM Wang, as shown in Appendices 1.1:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure nt-Ag</td>
<td>0.09</td>
<td>0.80</td>
<td>3.00</td>
</tr>
</tbody>
</table>

For nt-Ag (pure and segregated) metals, results with both kinked and perfect TBs have been included in the same fitting parameter, because the difference in HP behavior between the two cases was found to be negligible.

To find the HP fitting parameters for experimental results, we have considered the observation that both $\lambda$ and $d$ decreased at the same time. Figure 3.6 shows that it is
possible to find a linear relationship between $\lambda$ and $d$ over a specific range of $\lambda$. From the literature results by Bufford et al. [10] and Furnish et al. [29], we find:

$$\lambda/d = 0.062 \text{ for } \lambda < 36 \text{ nm} \quad (3.9)$$

Equation 3.9 was substituted into Equation 3.8 to fit the stress constant $\sigma_0$ on pure nt-Ag results, by assuming that the microstructure parameters, $K_{GB}$ and $K_{TB}$, were the same as those fitted from atomistic simulations for pure nt-Ag.

![Graph showing the ratio of $\lambda$ over $d$ for pure nt-Ag from past literature [10, 13, 29]](image)

**Figure 3.6: Ratio of $\lambda$ over $d$ for pure nt-Ag from past literature [10, 13, 29]**

As the HP plots are similar for materials with kinked and perfect TBs, the TB defects appear to have no impact for the most part. However, softening accompanied by a negative-slope HP region, is evident for materials with high density of kinked TBs when $\lambda \leq 2.8$ nm. Remarkably, between $\lambda = 2.8$ nm and 6.3 nm, we observe a third strength region where the HP slope is near zero. The strength in this previously
unobserved transition zone is independent of $\lambda$, suggesting that GB behavior mostly governs this transition. To our surprise, after the GB-dictated transition, the strengths of both pure and Cu-segregated nt-Ag with perfect TBs (i.e., ideal materials) reach a plateau without any sign of softening. These results indicate the existence of three distinct HP zones in “real world” materials, but only two for ideal ones.

At $d = 45$ nm, emission of extended Shockley partial dislocations, rather than GB sliding, is predicted to dominate the plastic deformation of nc-Ag. TBs actively strengthen this material by promoting hard slip mechanisms at dislocation – TB intersections, which is accompanied by numbers of non-Shockley sessile dislocations forming progressively as the $\lambda$ decreases (Figure 3.7).
The existing understanding [6, 30, 31] in pure nt-Cu is that the softening is associated with twinning partial dislocations nucleating from GB – TB junctions and propagating freely inside TBs, leading to a negative HP slope as the junction density increases. Our MD results in nt-Ag show very different softening mechanisms for the following reasons. First, we identify a slip transition accompanied by a breakdown of non-Shockley dislocations at $\lambda = 6.3$ nm (Figure 7 (d)) that does not match the simulated transition spacing for softening at $\lambda = 2.8$ nm. Second, with $\lambda = 2.8$ nm, we observe that most dislocation emissions occur outside GB-TB junctions along slip planes parallel to TBs (Figure 3.8).
before (0%) and after (7%) deformation are superimposed and shown in dark grey and yellow colors, respectively. Several dislocation nucleation sites outside GB-TB junctions are indicated with circles.

Figure 3.9 indicates that, with perfect TBs, the initial yield stress for dislocation emission mechanisms does not depend on \( \lambda \). On the contrary, reducing \( \lambda \) down to 1.4 nm markedly decreases the initial yield stress in the presence of kinked TBs.

**Atomic-scale study of GB plasticity**

To better understand the origin of a zero-slope HP region, we further conducted a detailed study of atomic-scale mechanisms of GB plasticity as function of \( \lambda \), Figure
3.3. We find from Figure 3.3 (a) to (e) that GB sliding in Cu-segregated nt-Ag is considerably intensified as $\lambda$ decreases. Remarkably, Figure 3.3 (e) demonstrates that GB sliding at 7% strain in nt-Ag with $\lambda = 3.5$ nm is doubled that of nc-Ag without TBs (when $d = 45$ nm). In fact, Figure 3.3 (f) reveals that the local GB shear-strain rates attain a maximum plateau of 0.0015 ps$^{-1}$ in Cu-segregated nt-Ag when $\lambda \leq 4.2$ nm, which is more than one order of magnitude higher than the strain rate imposed in the model overall. This phenomenon is governed by local GB stress effects, rather than by dislocation nucleation mechanisms, because it is not observed at the onset of plastic yielding, Figure 3.3 (e). During plastic flow from 5% to 7% strain, the maximum atomic stresses shift entirely from the grain interior to the GB region, as $\lambda$ decreases from 14.8 to 3.5 nm (Figure 3.10).
Figure 3. 10: Atomic-level tensile stresses ($\varepsilon_{xx}$) during plastic flow (5% applied strain). (a) and (b) MD snapshots of crystal slip and interface-mediated plastic deformation in Cu-segregated nt-Ag with $\lambda = 14.8$ and 3.5 nm, respectively. Stacking-faults and coherent TBs appear with a uniform light-grey color. Atoms at incoherent interfaces, GBs and TB kink-steps, are colored according to the local von-Mises shear strain rate, with the highest rates in red color. (c) and (d) The associated local tensile stresses $\varepsilon_{xx}$ with $\lambda = 14.8$ and 3.5 nm, respectively, showing that maximum stresses shift from TB-dislocation intersections inside grains to the GB region. (e) Average atomic tensile stress $\varepsilon_{xx}$ per GB atom inside the grain and in the GB region, respectively, as a function of twin spacing $\lambda$.

The transition to soft crystal slip modes parallel to TBs tends to accelerate this effect. The same GB-controlled mechanism is found with pure nt-Ag metals (Figure 3.11), but the GB shear rate and HP limit are lower, because GB stresses drop dramatically without impurity segregation, Figure 3.3 (g). These findings point at a direct relationship between HP limit and impurity-segregated local GB stresses – an observation that appears also consistent with recent experimental results in heavily alloyed nc metals [9].
Figure 3.11: Local von-Mises shear microstrain per atom accumulated from 5% to 7% applied strains in pure nt-Ag models with (a) $\lambda = 14.8$ and (b) 3.5 nm, respectively. The GB and dislocation plasticity mechanisms are the same as those in the Cu-segregated nt-Ag metals.

The modeling results above suggest that an ultrahigh strength is achievable in Cu-segregated nt-Ag materials with a $\lambda$ down to 2.8 nm (Figure 3.2 (d)). This affords opportunities for us to make a new class of high strength, high thermal stability, and high electrical conductivity materials. The microstructure length-scale is readily controlled by the content of Cu element (<1.0 wt.%). The small length-scales achieved are scientifically attractive as they match well with those used above to determine the zero-slope HP zone in MD simulations.

3.6 Conclusion

In summary, our work collectively demonstrates that nt metals exhibit two HP transitions that are unequivocally controlled by TB-defect softening and GB-controlled mechanisms, and that impurity-dictated strengthening is a viable approach for creating
super strong nanostructured metals concurrent with excellent electrical properties and high thermal stability. Our approach has clear advantages over existing heavy alloying [32] and hierarchical interface-design strategies [33] that may inevitably lead to the trade-off of strength and electrical conductivity, and is expected to be applicable broadly to other materials systems.

3.7 References


Zhang, C. W., T.T. Roehling, R.T. Ott, M.K. Santala, P.J. Depond, M.J. Matthews,
A.V. Hamza, T. Zhu, Additively-manufactured hierarchical stainless steels with high
CHAPTER 4. THE STRONGEST SIZE IN A NANOCRYSTALLINE
NANOTWINNED METAL

4.1 Abstract

The strongest size has long been used to characterize the transition grain size from grain-boundary strengthening to softening behaviors observed in nanocrystalline materials when the grain size decreases to the nanometer range. In nanotwinned metals and alloys, however, predicting the strongest size remains extremely challenging, because grain boundaries and twin boundaries become competing hardening and softening mechanisms. Furthermore, solute segregation, which is often used to stabilize the nanosized grains, complicates the above mechanisms. In this Chapter, large-scale hybrid Monte-Carlo / Molecular Dynamic simulations were used to systematically study the effects of grain size on the yield stress and flow strength in pure and Cu-segregated nanocrystalline nanotwinned Ag (nnt-Ag) metals. The strongest size is found to increase from 12 nm for pure nanocrystalline Ag to 20 nm for pure nnt-Ag, due to an increase in grain boundary sliding when twin boundaries are present. The transition grain size starts to decrease when a trace amount of Cu (0.8 at%) is segregated to the interfaces. Our simulations show that it is possible to ideally approach, and even exceed, the Hall-Petch strength limit in nnt-Ag with a grain size down to 6 nm, by solute segregation with Cu concentrations between 8 at. % and 12 at. %. For higher Cu contents (15 at.%), however, the predominant plastic deformation mechanism changes to shear-band induced softening. These results shed light on the effects of
solute segregation on grain-boundary-mediated plasticity mechanisms in nanocrystalline nanotwinned alloys.

4.2 Introduction

The concept of a “strongest” size was first brought up by Yip [1] to describe the grain size producing maximum strength in nanocrystalline (nc) materials, and is often associated with the mechanism transition from dislocation-mediated Hall-Petch-type strengthening [2, 3] to grain boundaries (GBs) induced softening, such as GB motions [4], GB sliding [5], GB migration [6] and grain growth [7]. Molecular dynamics (MD) simulations have suggested that the maximum flow stress occurred at a grain size between 10 nm and 15 nm in nc-Cu [4, 8], caused by a shift from dislocation plasticity to GB sliding. Based on the available experimental evidence, Conrad et al. [9, 10] have proposed to divide the flow stress mechanisms in face-centered cubic (fcc) Cu into three distinct grain size regimes: Larger than 1 μm, formation of dislocation cells; between 10 nm and 1 μm, dislocations restricted to slip planes; and below 10 nm, GB softening. Similar conclusions have also been drawn for body-centered cubic (bcc) metals such as Zn [11]. By contrast, in fcc Ag [12], the flow stress is more predominantly controlled by the dislocation density and dislocation pile-ups, whereas a softening region has not been observed for grain sizes as small as 9 nm. Furthermore, past MD simulation studies have shown that pure metals, such as nc-Al [13], nc-Mg [14], nc-Ni [15], have systematically exhibited a softening behavior below a critical grain size.
Beside GBs, coherent interfaces, such as twin boundaries (TBs), have been widely studied as both hardening and ductility mechanisms. Nanotwinned (nt) metals are formed by film growth, plastic deformation or thermal annealing [16]. Past MD simulation studies have shown that introducing nanotwins to different FCC metals resulted in either strengthening or softening, depending on the unstable stacking-fault energy [17, 18]. The hardening effect was observed in nt-Cu due to dislocations blocked by GBs and TBs [19-22], whereas twin-migration-induced softening was predicted in nt-Pd.

The strongest size was also shown to apply to nt-Cu metals as a function of twin size [23]. A strongest twin size was found at 15 nm, followed by softening, where the deformation mechanism changes from slip transfer across TB to the activity of pre-existing easy dislocation sources. Strain gradient theory [24] was used to model the dislocation pile-up zone around GBs and TBs in nt-metals [25]. For nt-Cu with 500 nm grain size, the strongest TB size was estimated to be 13 nm, which is in good accordance with experimental results from work in [23]. Deformation mechanisms were also studied by MD simulations for smaller grains with an average size of 10 nm and 20 nm [20]. At a critical TB spacing (~ 2.5 nm), the deformation mechanism shifted to dislocation-controlled softening resulting from the nucleation and motion of partial dislocation parallel to the twin planes. It was also shown that the strongest twin size was 1.25 nm and 2.08 nm for grain size 10 nm and 20 nm models, respectively. In conclusion, it appears that the smaller the grain size, the smaller the strongest twin size.
Furthermore, segregation of alloying elements to GBs has been shown to be an effective way to increase thermal stability and strength for nanostructured metals, where conventional solid solution strengthening is generally negligible [26-32]. Segregating proper amounts of solute atoms to interfaces can effectively reduce the excess free energy or free volume [27, 33]; or form fine precipitates inside GBs to increase grain stability [34].

FCC binary nc-alloys, such as Nb-doped Cu [28, 35], Ti-doped Ni [36], and Mg-doped Al [32], exhibit high segregation energy and GB strengthening with low-to-moderate solute concentrations. However, a higher amount of element segregation could also result in softening effects. The yield strength and flow strength for Ag-segregated Cu alloys were predicted to increase at low concentration; then decrease at higher Ag concentration due to GB thickening into an amorphous Ag film, accompanied by less GB sliding resistance [37].

Segregation is also an effective approach to suppress the softening behavior at smaller grain sizes and decrease the strongest size. Nc Ni-W alloys showed higher hardness and scratch resistance compared with pure nc-Ni. The breakdown of the Hall-Petch relation was shown to be suppressed by W addition [15]. The softening behavior of nanocrystalline Ni-W alloys was further investigated [38]. The maximum strength was found to be around 8 nm, as predicted by [15]. In nc-Ni alloys with Mo segregation, ultrahigh hardness above the Hall-Petch relationship was observed in nanograin samples [39] due to increased GB stability. Likewise, thermal desegregation
experiments in [40] have suggested that solute atoms contribute to the stability of Ag-W alloys.

Ultrafine-grained nanotwinned Ag (nt-Ag) have been experimentally prepared [41] with grain sizes between 150-200 nm and nanotwin spacings between 8-12 nm. Nanocrystalline nanotwinned Ag (nnt-Ag) of 45 nm grain size have been studied using Monte-Carlo / molecular dynamic (MC/MD) simulations [42]. Cu atoms segregate to the GBs and defective kinked TBs, resulting in increased stability against deformation. The yield stress was shown to rise substantially with low Cu content below 1 at.%. Critical stresses for incipient plasticity from GBs, kinked TB defects and dislocation nucleation were shown to increase as Cu concentration increases. However, the effects of grain sizes below 50 nm have remained unexplored so far.

In this Chapter, hybrid MC/MD simulations are used to study the stress-strain response of nc-Ag and nnt-Ag for different grain sizes from 6 nm up to 45 nm, with a particular focus on the effect of Cu microalloying on the strongest size in this materials system. Furthermore, for the smallest grain size (6 nm), the limit of Cu segregation strengthening, in comparison to the ideal Hall-Petch strength, is investigated by simulating the segregation behavior with higher Cu concentrations up to 15 at. %.

4.3 Methodology

Hybrid MC/MD simulations [33, 43] were performed to structurally and chemically relax large-scale and small-scale Cu-segregated nnt-Ag models at different Cu concentrations. The software LAMMPS [44] was used with an embedded-atom method (EAM) potential for Ag-Cu binary alloys by Wu and Trinkle [45]. Our own
simulations with this potential showed that the unstable and stable stacking-fault energies in pure Ag were equal to 115.3 mJ/m$^2$ and 16.6 mJ/m$^2$, respectively. We found that the generalized stacking-fault energy curve remained unchanged by randomly adding Cu atoms up to 5 at. % concentration, which indicated that solid solution strengthening was absent up to this limit. A Voronoi tessellation scheme was applied for structure generation with randomly distributed grain centers, random crystallographic orientations, and fully periodic boundary conditions, similar to our previous work [46]. GB atoms closer than 0.5 Å were removed. Structures of different grain sizes, 6, 7.5, 9, 12, 16, 20, 30, 45 nm, are created in cubic simulation boxes of 30, 37.5, 45, 60, 48, 60, 60, 90 nm in size; and with a total 1.5, 3.1, 5.3, 12.6, 6.5, 12.6, 12.6, 42.6 million atoms, respectively. Two types of models were created: nnt-Ag with each grain containing a uniform distribution of TBs spaced by 2.8 nm perpendicular to the [111] direction and nc-Ag with no TBs. The energy of each model was minimized by the conjugate gradient method. The structure was then relaxed under zero pressure using an isothermal–isobaric (NPT) ensemble at 450 K for 100 ps, then cooled to 300 K in 50 ps, and held at the same temperature for another 50 ps. Temperature was rescaled every 500 steps. The timestep was 5 fs, which was found to conserve the total system energy. The hybrid MC/MD approach used to simulate Cu atom segregation followed the method presented in [47]. It was run at 500 K for 1 million MD steps with a timestep of 2 fs and calls to MC every 10 MD steps. The temperature in MD was controlled by rescaling every 10 steps and pressure was maintained to 0 bar using a Berendsen barostat. The MC simulation part was carried out with a chemical potential
difference $\Delta \mu = -2.5$ eV, variance of Lagrange multiplier $\kappa = 100$. After segregation, the models were relaxed again in NPT ensemble under zero pressure from 500 K to 300 K for 100 ps and kept at 300 K for another 100 ps. The models were deformed in pure tension by stretching the simulation box at an engineering strain rate of $10^8 \text{ s}^{-1}$ along the x-direction until 10% strain. NPT ensemble at 300 K and zero pressure applied laterally along the z and y directions were used. The average tensile or shear stresses were computed by adding the corresponding Virial-theorem stress component over all atoms and dividing by the deformed volume of the simulation box. The 0.2% offset yield stress was determined by fitting the linear portion of the stress-strain curves up to the stress at which the first dislocations or GB plasticity were detected. The flow stress was determined by averaging stresses over 5% to 7% strain. Plastic deformation mechanisms were studied by common neighbor analysis (CNA) and atomic strain analysis in the software OVITO [48]. A network of three-dimensional cells of ~1 nm in wall thickness encompassing each GB interface in the model was created by Voronoi tessellation method [49] to identify a list of GB atoms before deformation.

To quantify the GB properties, an algorithm has been developed to find atoms located around GBs by creating a three-dimensional network of 1 nm in thickness, overlapping each interface. Other related works tend to use Common Neighbor Analysis (CNA) method to detect GB atoms instead. We did not use this method for two reasons. On one hand, Cu atoms are randomly distributed around GBs, not segregated locally inside GBs. On the other hand, during plastic deformation
simulation, defect atoms in dislocation cores inside the grain interior will be recognized as GBs if CNA method is used. GB network can be tracked during plastic deformation.

Furthermore, GB atoms are more disordered than crystalline ones in the grain interior. The local atomic motion inside GB accommodates the local stress more easily due to a larger amount of free volumes available in pure materials. It is established that excess free volume inside GBs controls the strength and stability of GBs against plastic deformation [37]. We defined the excess free volume (EFV) per GB atom based on the approach given in [37]. Each atom inside the GB network was analyzed using the Voronoi modifier in Ovito to calculate its atomic volume. The EFV was calculated using Eq. (1):

$$EFV = \sum \frac{V_{GB} - N_{Ag} \times V_{Ag} - N_{Cu} \times V_{Cu}}{N_{Ag} + N_{Cu}}$$

(1)

where $V_{GB}$ is the atomic volume for each atom inside GBs, $N_{Ag}$ and $N_{Cu}$ is the number of Ag and Cu atoms inside GBs respectively, $V_{Ag}$ and $V_{Cu}$ are the atomic volumes of Ag and Cu atoms in the single crystalline phase, respectively.

The simulations were performed on the high-performance supercomputers SuperMIC at the Extreme Science and Engineering Discovery Environment (XSEDE) [50] and Cori at the National Energy Research Scientific Computing Center (NERSC).

4.4 Results and Discussion

4.4.1 Influence of TB and Impurity Segregation on the Strongest Size

4.4.1.1 Chemical and Structural Analysis of GB Networks
Figure 4.1 (a)-(c) show the atomistic structures of nnt-Ag models of 6 nm, 16 nm and 45 nm in grain size. Atoms in perfect fcc arrangement are colored in blue, coherent TBs in red color and other defects such as GBs in yellow color. Also, nc-Ag equivalents with no TBs were studied, but not shown here. Figure 4.1 (d)-(f) show the corresponding Cu distribution in structures segregated to 0.8 at. % Cu using hybrid MC/MD simulations. The coloring of Cu atoms follows the same CNA-based method as in Figure 4.1 (a)-(c). Cu atoms are primarily distributed around GB structures, forming a 3D network. Even though the overall Cu concentration is the same at 0.8 at.% across models, the distribution of Cu atoms varies as a function of grain size. At 6 nm grain size, most Cu atoms are segregated inside GBs. At 45 nm grain size model, however, GBs are saturated with Cu atoms. A fraction of Cu atoms that are randomly distributed in the grain interior in fcc and hcp sites is noticeable. Cu solute atoms show no preference to segregate into TBs. It is important to note, however, that the TBs considered in this study are perfect, so there are no TB defects to form solute attraction sites, as in [42].
Figure 4.1: Atomistic models of nnt-Ag with a constant TB spacing of 2.8 nm. CNA snapshots for nnt-Ag models with an average grain size of (a) 6 nm, (b) 16 nm and (c) 45 nm. Cu atom distribution after hybrid MC/MD simulations to 0.8 at. % for a grain size of (d) 6 nm (e) 16 nm and (f) 45 nm. Atoms in perfect fcc arrangement are colored in blue, coherent TBs in red color, GB and TB defects in yellow color. (g) Excess free volume per GB atom. (h) GB atomic fraction and...
local Cu concentration in GB network. The inset shows an example of GB network structure used for calculation in the 16 nm grain size model.

Figure 4.1(g) shows the EFV as a function of grain size $d$. The EFV is higher in pure metals than in Cu-segregated ones, which is consistent with the literature [37]. In pure metals, as $d$ increases, the EFV increases moderately and quickly saturates to a constant value of 0.85 Å$^3$ per GB atom. We conclude that the grain size has a little-to-no intrinsic effect on the EFV. On the contrary, in Cu-segregated metals, we surprisingly find that the EFV decreases markedly from 0.7 to 0.45 Å$^3$ per GB atom, as $d$ increases. To understand this phenomenon, we represent the local Cu concentration inside the GB network in Figure 4.1(h). The local Cu concentration in Cu-segregated nnt-Ag reached 7.7% at $d = 45$ nm, but is reduced to only 1.8% at $d = 6$ nm. Here, it is important to note that materials with a larger grain size exhibit higher local concentration because the percentage of GB atoms is smaller. In fact, Figure 4.1(h) shows that the GB atom percentage follows a $1/d$ relation. In conclusion, the pronounced grain size effect on EFV relates to the lower local concentrations when the GB fraction increases as $d$ decreases.

4.4.1.2 Initial Yield Behavior
Figure 4.2: Grain size and Cu segregation effects on simulated stress-strain curves. (a) Pure nc-Ag. (b) Pure nnt-Ag. (c) 0.8 at.% Cu-segregated nnt-Ag.

After hybrid MC/MD simulations and relaxation at 300 K, simulations of tensile deformation up to 10% are performed. The 0.2% offset yield stresses of all models are summarized in Figure 4.3 (b). In pure models, the yield stress is hardly affected by grain sizes and remains almost constant. Also, it is found that the effect of TB on yielding is small. In Cu-segregated models, however, the yield stress increases dramatically as the grain size increases. To understand this occurrence, it is important to point out that, the yielding behavior of Cu-segregated nnt-Ag is highly dependent on local Cu concentration. With 0.8 at.% Cu segregated models, Figure 4.2 (c) shows that a yielding overshoot behavior is more apparent in simulations with larger grain sizes, because the local Cu concentration is higher, as shown in Figure 4.1(h). The present simulations therefore support the theory that higher Cu inside the GB network increase GB strength by reducing the EFV. More specifically, the EFV analysis in Figure 4.1 (g)
shows that for pure models, the grain size does not affect the EFV as much as local Cu concentration does. As discussed above, the EFV remains almost constant in pure models, but decreases markedly as grain size increases in Cu-segregated ones. Therefore, the yield stress required to initiate dislocation nucleation is higher at larger grain size, due to higher local Cu concentrations.

![Graph showing yield stress as a function of grain size.](image)

**Figure 4.3**: 0.2% offset yield stress as a function of grain size.

4.4.1.3 Hall-Petch Strengthening to Softening Behavior

The flow stresses are calculated by using stress data averaged between 5% - 7% applied strain, as shown in Figure 4.4, as a function of grain size $d$. 

91
Figure 4.4: Flow stress averaged between 5% to 7% strain, as a function of grain size. Vertical arrows indicate where the strongest size occurs.

The Hall-Petch relation was fitted on the atomistic results using the equation:

\[ \sigma = \sigma_0 + \frac{K_d}{\sqrt{d}} + \frac{K_\lambda}{\sqrt{\lambda}} \]  

where \( \sigma \) is the flow stress, \( \sigma_0 \) is the friction stress, and \( \lambda \) is the TB spacing (\( \lambda = 2.8 \) nm), \( K_d \) is the Hall-Petch constant for GBs and \( K_\lambda \) is the Hall-Petch constant for TBs. The data are fitted separately for pure and Cu-segregated models. The fitting constants obtained are shown in Table 1. The parameters \( \sigma_0 \) and \( K_d \) remained identical between
pure nc-Ag and pure nnt-Ag models. By contrast, after segregation, an increase in $\sigma_0$ of ~0.2 GPa is observed, while $K_d$ and $K_\lambda$ remain the same. The absence of a dependence of $K_d$ and $K_\lambda$ on Cu content can be attributed to the low concentration of Cu remaining in solution inside the grains [51].

Table 4.1: Hall-Petch fitting constants obtained from MD simulations.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_0$ (GPa)</th>
<th>$K_d$ (GPa·nm$^{0.5}$)</th>
<th>$K_\lambda$ (GPa·nm$^{0.5}$)</th>
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<td>Pure nc-Ag models</td>
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</tr>
<tr>
<td>Pure nnt-Ag models</td>
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<td>Cu-segregated nnt-Ag models</td>
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<td>1.9701</td>
<td>0.5029</td>
</tr>
</tbody>
</table>

The plastic deformation mechanisms at different grain sizes for Cu-segregated nnt-Ag of 0.8 at. % are presented in Figure 4.5. The atomic von-Mises shear strain per atom was computed and rendered from 0 to 0.1. The yielding mechanism is studied using applied strains between 2-4%, while plastic flow mechanisms used strains between 5-7%. At $d = 6$ nm, GB plasticity is dominant with dislocation nucleation for both yielding and plastic flow deformation. At $d = 20$ nm, dislocation nucleation and propagation are dominant in both yielding and plastic flow deformation. The same mechanisms were observed for pure nc-Ag and pure nnt-Ag metals but have not been repeated here for conciseness.
Figure 4.5: Plastic deformation mechanisms based on atomic shear strain ($\varepsilon_{VM}$) for small (6 nm) and large (20 nm) grain sizes in 0.8 at.% Cu-segregated nnt-Ag. (a) Yielding mechanisms between 2% to 4% applied strain. (b) Flow stress deformation mechanisms between 5% to 7% applied strain.

For pure nc-Ag, the Hall-Petch strengthening region extends from 12 nm to 45 nm and the strongest size is 12 nm. For pure nnt-Ag, the strongest grain size is close to 20 nm. For Cu-segregated nnt-Ag at 0.8 at.% Cu, this value decreases to 16 nm. In Figure 4.6 (a), the amount of average atomic von Mises shear strain in GB during deformation are calculated for pure nc-Ag, pure nnt-Ag and Cu segregated nnt-Ag. The amount of GB motion during plastic deformation is compared between the three models by averaging the atomic shear strain rate inside GB divided by the averaged flow stress.
It is shown in Figure 4.6 (b) that GB motion is higher in the pure nnt-Ag model than the pure nc-Ag model at a grain size of 12 nm surprisingly. Introducing nanotwins results in more GB sliding strain and an increase in the strongest size. For the Cu-segregated nnt-Ag model, a slight decrease in GB sliding is observed, indicating GB strengthening from solute segregation.

In Figure 4.4, an increase of strongest size in Cu-segregated nnt-Ag is noticeable when compared to the pure nnt-Ag models. A model for predicting the strongest size after solute segregation has been proposed by Schuh et al. [15]. This theory has adapted here as follows:
\[ \frac{d_{\text{alloy}}}{d_{\text{pure}}} \approx \left[ \frac{D_{\text{Ag-Cu}}}{D_{\text{Ag}}} (1 - c) + c \right]^{2/7} \approx c^{2/7} \] (3)

where \(d_{\text{alloy}}\) is the strongest size of the alloy systems, \(d_{\text{pure}}\) is the strongest size in pure systems, \(D_{\text{Ag-Cu}}\) is the diffusivity of Cu in Ag, \(D_{\text{Ag}}\) is the diffusivity of Ag and \(c\) is the Cu concentration. \(D_{\text{Ag-Cu}} / D_{\text{Ag}}\) is estimated to be about \(10^{-7}\) and thus is considered negligible [53, 54]. Numerically, this model predicts that a concentration of 1.5 at.% Cu (which is double that of 0.8 at. %Cu used here) would decrease \(d_{\text{alloy}}\) to 6 nm, which is qualitatively consistent with the present results.

4.4.2 Segregation Strengthening Beyond the Hall-Petch Limit

To further understand how far Cu segregation can contribute to the strengthening of nnt-Ag at the smallest 6 nm grain size, hybrid MC/MD simulations were performed to apply higher Cu concentrations up to 15 at. % as shown in Figure 4.7. In Ag-doped nc-Cu [37], Ag solute atoms were predicted to segregate to GBs. Higher solute concentrations formed thick layers of Ag atoms at interfaces. In this study, the solute atom distribution is different and tends to be segregated to both GBs and grain interiors simultaneously, with a preference to segregate to GBs. After Cu segregation, the majority of atoms inside GBs are still Ag atoms. For example, when
the total Cu concentration reaches to 15 at.% for nnt-Ag of 6 nm grain size, the local Cu concentration is 19 at.% in GBs, compared with 14 at. % in the grain interior. No Cu layers are formed inside GBs at high concentrations in this study. Figure 4.7 (d) shows that the EFV decreases continuously below zero as more Cu atoms are segregated locally to GBs as shown in Figure 4.7 (e). The local Cu concentration inside the grains is always lower than inside the GBs.

Figure 4.7: Atomistic snapshots of common neighbor analysis (CNA) and hybrid Monte Carlo / Molecular Dynamic (MC/MD) simulations for nnt-Ag with 6 nm grain size. (a) CNA snapshots before MC/MD simulations. Cu atom distribution after hybrid MC/MD simulations to (b) 2.4 at. % and (c) 15.0 at.%. (d) Excess free volume per GB atom and (e) local Cu concentration in GB network and grain interior for different Cu concentrations. Atoms in perfect fcc arrangement are colored in blue, coherent TBs in red color, GB and TB defects in yellow color.
Figure 4.8 (a) shows the simulated stress-strain curves of models with different Cu concentrations up to 15 at.%. An overshoot in the stress-strain curves is observed as Cu concentration increases. The dependence of EFV on Cu concentration, as shown in Figure 4.7 (d) governs this type of yielding behavior, Fig 4.7(d). Metals with larger grain sizes have higher local Cu concentration and lower EFV which, in turn, leads to higher GB strength and yield strength.

Figure 4.8: Mechanical behavior of 6 nm grain size nnt-Ag with different Cu at.% segregated by hybrid MC/MD simulations. (a) Simulated stress-strain curves. (c) Flow stresses averaged between 5% to 7% applied strain. The ideal HP strength represents the theoretical estimate from HP relation Equation (2) with \( d = 6 \) nm.

Figure 4.8 (b) shows the flow stress calculated by averaging stress data between 5% and 7%. The flow stress is shown to increase with Cu concentration and to plateau at concentrations above 8 at. %. It is shown in Figure 4.8 (b) that Cu contents of 5 at.% or higher result in higher flow stresses that are slightly above the ideal Hall-Petch limit as predicted from pure nnt-Ag models from Equation (2) and Table 4.1 using \( d = 6 \) nm. The flow stress increases from 1.33 GPa for the pure model to 2.11 GPa for the 8.0
at.% model, followed by softening for Cu concentrations above 12 at.%. The minimum Cu concentration required to retain the Hall-Petch relation to 6 nm is about 5 at.% Cu in total. The selective distribution of Cu atoms inside our nnt-Ag models is one reason for the difference with the theoretical prediction of 1.5 at.% from Equation (3). Equation (3) assumes equal Cu atom distribution between GBs and grain interior. A higher total Cu concentration is therefore needed for GB strengthening in Ag/Cu alloys, since grains are more depleted in solute elements.

To further investigate the plastic deformation mechanisms after Cu segregation, yield deformation between 0-4.5% strain and plastic flow deformation between 5-7% strain are shown in Figure 4.9 by using the atomic strain analysis in the software Ovito. The onset of yielding is marked by dislocation nucleation at all concentrations, with different levels of GB plasticity. In Figure 4.9 (a), the yielding for the pure nnt-Ag model is accompanied by GB sliding and dislocation nucleation simultaneously. For Cu-segregated models, however, the yielding is mostly controlled by dislocation initiation as observed in Figure 4.9 (b) and Figure 4.9 (c). Comparing model with 8 % Cu and 15 % Cu, atom shuffling is observed in GBs suggesting a continuous strengthening effect with higher Cu concentrations. The plastic flow deformation mechanism is controlled by GB sliding and dislocation emission for the pure model, as shown in Figure 4.9 (d). As the Cu concentration rises to 8%, Figure 4.9 (e), less GB plasticity is observed but a noticeable level of dislocation activity is present. In Figure 4.9 (f), when the Cu concentration reaches 15 at.%, the deformation mechanism
completely changes to shear banding, with localized dislocation emissions inside each grain. Further GB strengthening by Cu segregation makes dislocation nucleation from GBs more difficult. Therefore, less geometrically necessary dislocations are formed to accommodate the plastic deformation at GBs. Consequently, GB strengthening does not always produce higher flow stresses due to this change of deformation mechanism.

Figure 4.9: Deformation mechanisms of grain size 6 nm nnt-Ag at different Cu concentrations. Yielding mechanisms are shown between 0% to 4.5% strain for (a) pure model (b) 8.0 at.-% model and (c) 15.0 at.-% model. Plastic deformation mechanisms are shown between 5% strain to 7% strain for (d) pure model (e) 8.0 at.-% model and (f) 15.0 at.-% model. Atomic shear strain snapshots are rendered with scalebar from 0 to 0.1.
Microalloying is an approach to increase the yield stress of nnt-Ag and nc-Ag. But this study suggests that the suitable amount of solute is highly dependent on the grain size. The atomic percentage of GB is dependent on the grain size, at same global Cu concentration, the final local Cu concentration after hybrid MC/MD simulation is dependent on the grain size as well. As we can see from Figure 4.1 (h), as the grain size decreases, the percentage of GB is increased. Segregating the same Cu amount at different grain sizes result in less local Cu concentrations for smaller grain sizes. In other words, strengthening effects at smaller grain sizes require more solute Cu atoms.

The present study suggests that heavy alloying is necessary for maintaining the HP relationship without softening at small grain sizes. But segregation should be kept at a carefully chosen concentration range. A higher amount of alloying does not guarantee better mechanical properties. In our work, as shown in Figure 4.8 (b), flow stress plateaus at higher Cu concentration above 5 at.%. Further Cu additions would become detrimental, as the plastic deformation would be at risk to shift to shear banding mechanisms and associated with softening.

4.5 Conclusions

In this chapter, we have applied hybrid MC/MD simulations to study the effects of grain size and Cu concentration on strengthening and softening mechanisms in nnt-Ag alloy with and without Cu impurities. The Hall-Petch relation and associated plastic deformation mechanisms were studied in detail for pure nc-Ag, pure nnt-Ag and nnt-Ag
with 0.8% Cu. We found that the local solute Cu concentration inside the GBs played a dominant role in controlling the yield stress; higher Cu concentration increased the yield stress dramatically. Plastic flow deformation was dominated by GB sliding at small grain sizes; and dislocation-mediated plasticity at large grain sizes. For a small grain size of 6 nm, the ideal Hall-Petch strength limit can be retained for a Cu concentration of 5 at. %. However, Cu concentrations as high as 15 at. % were found to change the deformation to shear-band-induced softening. We have shown that it is possible to increase the strength of nanostructured metals by GB segregation above the theoretical HP limit where a softening behavior is usually observed.

Acknowledgments

Support from U.S. Department of Energy Grant No. DE-SC0016270 and the computational resources provided by Extreme Science and Engineering Discovery Environment (XSEDE) supported by NSF grant number ACI-1053575, and National Energy Research Scientific Computing Center (NERSC) are gratefully acknowledged.

4.6 References


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CHAPTER 5. MAJOR CONCLUSIONS AND FUTURE RESEARCH

This thesis provided atomistic insight into the mechanical behavior of nanocrystalline nanotwinned (nt) Ag-Cu alloys. Cu solute segregation in nanotwinned Ag (nt-Ag) metals was simulated using large-scale hybrid MC/MD simulations. The effects of (1) Cu segregation, (2) intrinsic TB defects, (3) twin size and (4) grain size on plasticity and associated deformation mechanisms have been studied systematically by performing tensile simulations using classical molecular dynamics. The main conclusions can be drawn as follows.

**TB defect-induced plasticity.** Solute GB segregation has been shown to be an effective way to increase the stability and yield strength of intrinsic kink-like defects in “real-world” nt-Ag metals containing trace amounts of solute atoms (< 1.0 at.% Cu). TB step defects and GBs were found to be the preferential sites for Cu atoms to segregate. The TB resistance to detwinning by defect migration was shown to increase dramatically with Cu segregation. Also, it was found that segregation changed the plastic deformation mechanism of kink-step defects from migration to kink-activated crystal slip and that the tensile yield strength was directly associated with the Cu-dependent critical stress for dislocation nucleation at GBs and TB defects. In summary, this thesis points to the importance of microalloying to achieve superior strength and microstructure stability in nnt metals.
**Twin size effects.** Three distinct strength regions were discovered as twin size decreases, delineated by normal Hall-Petch strengthening with a positive slope, the GB-dictated mechanism with near-zero Hall-Petch slope, and the TB defect-induced softening mechanism with a negative Hall-Petch slope. Together with the work from experimental collaborators, it was shown that impurity-strengthening is a viable approach for both superior mechanical strength, higher thermal stability and excellent electrical conductivities. In summary, microalloying was shown to obtain a clear advantage over heavy alloying, where the trade-off between strength and electrical conductivity will be expected. The idea of microalloying can be applied broadly to other alloy systems.

**Grain size effects.** The “strongest” size for pure nt-Ag was found equal to 20 nm. The controlling plastic deformation mechanism changed from dislocation nucleation to GB-mediated softening. This transition decreased to 16 nm when 0.8 at.% of Cu solute was segregated to the interfaces. It was found that segregation of higher Cu concentrations (> 1 at.%) continued to strengthen nnt-Ag metals with smaller grain sizes down to 6 nm, which is well below the strongest size of 20 nm in the pure metal. The local Cu concentration analysis showed a continuous GB strengthening effect up to 12 at.% Cu. For very high Cu content $\geq 15$ at. %, however, the predominant plastic deformation mechanism changed to shear-band induced softening, which led to poorer strength performance. In summary, there is an optimum Cu concentration for
segregation to effectively strengthen the GBs and the overall mechanical behavior, at smaller grain sizes.

**Brief Outlook for Future Research.** Based on the conclusions of this thesis, three potential axes can be proposed for future research.

First, more complex kink defects in atomistic models should be prepared to further study their effects on mechanical properties and plastic deformation mechanisms. Kink step defects in atomistic models for this thesis were prepared with identical height (0.7 nm) and separation distance (10 nm). Experimentally, however, the kinks are more randomly distributed in both height and separation. During our simulations, some defects annihilated with nearby kinks to form a perfect twin boundary. If kinks were considered as more randomly distributed, more complex kink/kink or kink/dislocation interaction could be examined, and new deformation mechanisms could be discovered.

Second, different alloy systems should be studied by simulations to find new solute distribution patterns. In this study, solute atoms in nt-Ag followed a homogeneous random distribution around grain boundaries. Experimentally, however, it was observed that solute atoms could segregate to GBs to form either a thick layer or precipitates around the interfaces. Effect of heterogeneous solute distribution or precipitation on mechanical properties such as strength, deformation mechanism, grain boundary sliding, can be further studied in the future using the computational approach.
described in this thesis. A caveat, however, is that new interatomic potentials should be
developed for accurately simulating segregation or precipitation behavior at interfaces.

Third, the effects of heavy alloying and segregation should be further studied
using atomistic simulations. Microalloying effect below 1.0 at. % has been the focus of
this study. At higher solute concentration, more Cu atoms could be segregated to GBs
in nt-Ag. For nt-Ag of 6 nm grain size, the deformation mechanism was observed to
change from dislocation nucleation to shear-banding behavior. Further work on the
shear-banding deformation mechanism transition should be carried out across different
grain sizes and solute concentrations to build a more solid theoretical model for
predicting the optimal mechanical behavior.
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APPENDICES

Content:

1. Supporting Information from Co-authors in Nature Materials submission
2. LAMMPS Script for MC/MD simulations
3. LAMMPS Script for Tension Simulation
4. Python Script for Identification of a Three-dimensional GB Network
1. Supporting Information from Co-authors in Nature Materials submission

A. Experimental Results

Abstract

We synthesized ultrahigh hardness nanocrystalline-nanotwinned Ag (3.05 GPa — 42% higher than the current record) by selectively segregating trace concentrations of Cu (<1.0 wt.%) — a solute that is predicted to have no strengthening effect when the content is below 3.0 wt.%. The microalloyed materials remain stable up to 653 K; i.e., 215 K better than for pure nanotwinned Ag, with the retention of excellent electrical conductivity. These exceptional properties break the existing trade-off between strength and electrical conductivity.

Materials and Methods

Materials synthesis. Thin film samples of pure nt-Ag and Cu-microalloyed nt-Ag were synthesized by magnetron sputtering onto <100> oriented Si wafers. Three 50 mm diameter Ag targets were arranged in a confocal geometry to sputter onto the 152-mm diameter substrate, which was rotated at 15 revolutions per minute and cooled with liquid nitrogen. For the microalloyed samples, a fourth target of Cu metal, 76 mm in diameter, was arranged in a confocal geometry outside the circle of Ag targets. The distance from the Ag and impurity sputtering targets to the center of the substrate were 120 and 156 mm, respectively. For all of the sputtering runs, the base pressure was < 5 × 10⁻⁸ torr and the working pressure was 5 mtorr of Ar. The three sputtering guns with Ag targets were operated at 300 W for each deposition run, while the sputtering gun with the Cu target was operated at 20 to 100 W for the different runs. Our extensive
transmission electron microscopy characterizations of as-synthesized pure nt-Ag and Cu-mixed nnt-Ag materials indicate that the grain size of these films depends on the film thickness, whereas the average twin spacing ($\lambda$) remains relatively constant throughout the thickness. For consistency, the grain size reported in the main text is measured from the bottom side of the films except where noted.

**Impurity level analysis.** The compositions of the as deposited films were measured by electron microprobe analysis using a JEOL JXA-8200 (Peabody, MA, USA) wavelength/energy dispersive combined microanalyzer. In order to map out the composition of a large area, a dot-by-dot scan method (2mm×2mm) was used.

**Thermal annealing.** Pure nt-Ag and Cu-microalloyed nnt-Ag samples were annealed using a tube furnace (with 1-inch diameter quartz tube) under 100-sccm Argon (ultrahigh purity) flow at temperatures of 373 K, 423 K, and 473 K. Ramping rate is 10 K/min. They were held at target temperatures for 30 minutes and furnace cooled back to room temperature.

**Nanoindentation.** Two types of films were used in the nanoindentation experiments. The first type has the thickness of 1 μm, which contains equiaxed grains from the cross-section. The second type has a thickness of 2 μm, which contains a mixture of equiaxed and columnar grains. The indentation depths for the first and second types of films are 100 nm and 200 nm, respectively. Nanoindentation experiments were performed using Hysitron TI900 Tribo Indenter (Eden Prairie, MN, USA) equipped with a Diamond Berkovich tip. Displacement control mode was adopted to make sure the hardness values for different samples were measured at
similar contact depth. We find that the hardness values of nt-Ag and nnt-Ag are stabilized at an indentation depth of 200 nm for 2μm-thickness samples (Figure 5), consistent with the literature reports [1,2]. It was also found that the hardness variations obtained from 1μm- and 2μm-thick samples are relatively small. Therefore, the hardness values reported in this work are from 2μm-thick samples. Three segments were set for the load profile with 20s loading, 5s holding and 20s unloading followed by 40s drift correction period. Oliver-Pharr method was used to extract the effective modulus and hardness. The changes of surface morphology and roughness after thermal annealing were measured using the scanning mode of the nanoindentation system. A constant load of 2 μN was applied on the Berkovich indenter tip. The scanning frequency is 1 Hz.

**Electrical resistivity measurements and calculations.** Both pure nt-Ag and nnt-Ag-0.81wt.%Cu thin films (2 μm thick) were cut into the standard Hall-bar configuration with the dimensions of 2.14 × 0.56 mm² (length × width). The four leads were attached with silver paint. The resistance measurements were performed with a Janis ST-500 probe station (Woburn, MA, USA) and a home-made liquid helium cryostat. The DC current of 1 mA was applied over a temperature range of 4 to 339 K in our experiments. The resistivity of a metal can be written as \( \rho_o = m/(ne^2\tau_0) \), where \( m=0.99m_e \) is the effective mass of electron, \( m_e=9.11\times10^{-31} \) kg the electron mass, \( n=5.85\times10^{28} \) m⁻³ the electron density of Ag [3], \( e=1.60\times10^{-19} \) C the electron charge, and \( \tau_0 \) the relaxation time. The Fermi velocity \( V_F \) of Ag is 1.39×10⁶ m/s [3]. The mean electron free path induced by the structural scattering can thus be calculated as \( \lambda_o=V_F\tau_0 \)
**In-situ X-ray diffraction (XRD) heating analysis.** For the in situ XRD experiments, free-standing films ~50 μm in thickness were prepared using a 180-minute deposition time. The in-situ XRD experiments were performed with a Panalytical X’Pert Pro Diffractometer with Co Kα radiation and X’Celerator detector. The samples were heated in an Anton-Paar HTK 1200N hot-stage in flowing helium gas at a constant rate of 5 K/min. The thermal expansion of the stage was accounted for by offsetting the sample z-height during heating. The XRD scans were collected every 2 minutes over a selected 2θ range to include the [2, 4] and {200} reflections. For 50 μm thick films, the grain sizes measured from the top surface are ~450 nm for pure nt-Ag, and ~300 nm for Cu-mixed nt-Ag.

**TEM specimen preparation and characterizations.** Plan-view transmission electron microscopy (TEM) specimens were prepared using ion milling at liquid nitrogen temperature. The ion milling was done on the free-side (top) of the films to examine the structure closer to the substrate side (film bottom). The average grain size of the pure nt-Ag and Cu-doped nt-Ag samples were measured from the planar view specimens using an FEI Tecnai G2 F20-XT TEM operated at 200KV. Some cross-sectional samples were also examined by a Philips CM-30 TEM operated at 300 KV. The cross-sectional TEM samples were prepared by a focused-ion-beam (FIB) machine (FEI Nova 600 Dual-Beam FIB, Oregon, USA). The average grain size (d) and average twin spacing (λ) shown in Figure 1 (c) and 1 (d) were counted from 149 grains and 154 TBs, respectively.
We have successfully fabricated a series of Cu-microalloyed (<1.0 wt.%) nnt-Ag samples (Table 1).

Table 1: Some high-purity nnt-Ag and microalloyed nnt-Ag synthesized in this study

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>d (nm)</th>
<th>λ (nm)</th>
<th>Impurity level (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nnt-Ag</td>
<td>147±15</td>
<td>8.0±2.0</td>
<td>0</td>
</tr>
<tr>
<td>nnt-Ag-0.19Cu</td>
<td>55±4</td>
<td>5.2±2.3</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>nnt-Ag-0.63Cu</td>
<td>53±8</td>
<td>4.4±1.8</td>
<td>0.63±0.03</td>
</tr>
<tr>
<td>nnt-Ag-0.81Cu</td>
<td>49±15</td>
<td>3.6±1.5</td>
<td>0.81±0.04</td>
</tr>
</tbody>
</table>

The strongest material has an average d of 49 ± 15 nm and twin spacing λ = 3.6 ± 1.5 nm. Surprisingly, we find that these materials retain a continuous HP strengthening behavior, well beyond the normal HP breakdown seen in other nt metals [5].
Figure 1: Microstructure of Cu-impurity-mixed nanocrystalline-nanotwinned Ag (nnt-Ag) synthesized by magnetron sputtering. (a) Plan-view TEM image of nnt-Ag-0.81wt.% Cu sample. (b) Cross-sectional view of high-density growth twins of the same sample in A. The image is taken at ~1.5 μm film thickness. The inset is a high-resolution TEM image of incoherent twin boundaries (ITBs) and twin steps (or kinks). C. and D. The grain size (d) and twin spacing (λ), respectively.

The as-synthesized nnt-Ag has mostly equiaxed grains from plane-view transmission electron micrograph (TEM), Figure 1 (a) and Figure 2 (a)-(b). High-density growth twins are evident from cross-sectional TEM images, Figure 1 (b) and Figure 2 (c).
Figure 2: The microstructure of nanocrystalline-nanotwinned Ag (nnt-Ag) with various impurity levels. A. and B. Plan-view TEM images of 0.19 wt.% and 0.63 wt.% Cu-microalloyed nnt-Ag. C. Cross-sectional TEM view of 0.19 wt.% Cu-mixed. Note that this cross-section TEM image was taken at ~5 µm film thickness where the columnar grains become more evident.

TB defects are stable at this λ as small kink steps and incoherent TBs are also visible under high-resolution TEM, inset of Figure 4 (b). Through in-situ x-ray diffraction heating experiments, we find that the microstructure of pure nt-Ag (d=147±15 nm, λ=8.0±2.0 nm) becomes unstable at 438 K (Figure 3).

Figure 3: The evolution of {111} peak width at half maximum (FWHM) for nt-Ag and nnt-Ag-0.19wt.% Cu as a function of heating temperature during in-situ x-ray diffraction (XRD) analysis.
The FWHM is normalized against the 298 K value. The arrows in the figure point at the onset of thermal instability.

In contrast, that of a 0.19±0.02 wt.% Cu-mixed sample remains unchanged up to 653 K; i.e., 215 K higher than for pure nt-Ag. The much higher thermal stability of the impurity-mixed nnt-Ag is impressive, considering that this material has much smaller $d$ (55±4 nm) and $\lambda$ (5.2±2.3 nm).

![Figure 4: Hardness and electrical conductivity of Cu-impurity-mixed nnt-Ag. A Hall-Petch plot for nanoindentation hardness of pure nt-Ag and Cu-mixed nnt-Ag metals synthesized, along with references for high-purity nt-Ag [4, 6] and a range of values for well-annealed bulk Ag crystals with different dislocation density contents [7]. A continuous strengthening behavior is observed up](image-url)
to the smallest length scale we have investigated \((d=49\text{ nm}, \lambda=3.6\text{nm})\). Theoretical prediction from the normal Hall-Petch relationship (Equation 3.8) is represented with a solid line.

The hardness measurements of as-deposited pure nt-Ag and Cu-mixed nnt-Ag samples, along with past references for high-purity nt-Ag [4, 6] and well-annealed bulk Ag crystals [7], are shown in Figure 4 (a) and Figure 3.7 (a).

![Figure 5](image)

**Figure 5**: Hardness variations as a function of indentation depth, film thickness, and different microalloyed elements. A. Hardness as a function of indentation depth observed for nnt-Ag-0.63wt.%Cu sample (2 μm thick). The hardness reaches a stable value at ~200 nm depth. B. The same as a except that the film thickness is 1 μm. C. Hardness at 200 nm indentation depth as a function of film thickness (1 μm vs. 2 μm).

The HP relationship (Equation 3.8) shows good quantitative agreement with the experimental results. These measurements indicate a continuous increase in hardness down to the smallest \(d\) and \(\lambda\) synthesized. This continuous HP strengthening down to \(\lambda\sim 3.6\text{ nm}\) is significant from several aspects. First, hardening down to \(\lambda \sim 3.8\text{ nm}\) has been reported in a covalent-bonded material [8], the mechanism of which was attributed to the quantum confinement effect that is considered impossible in bulk metals [8, 9]. Second, a softening transition at \(\lambda = 12-37\text{ nm}\) was previously observed.
experimentally in nt-Cu with large equiaxed grains [10]. Yet we observe a continuous HP strengthening in Cu-mixed nnt-Ag films containing either small equiaxed grains (for 1 µm thickness film) or a mixture of small equiaxed- and columnar-grains (for 2 µm thickness film, see Figure 6 (a)-(b).

Figure 6: Microstructure and surface morphology of Cu-mixed nnt-Ag before and after 423 K annealing. A. and B. Focused-ion-beam images of as-deposited and 423 K annealed nnt-Ag-
0.63wt.% Cu. C.-E. and F.-H., atomic force microscopy (AFM) images of nt-Ag and nnt-Ag-0.81wt%Cu before and after annealing at a temperature up to 473 K. The whole annealing was completed in Ar environment for 1 hour. The scale bar in all the figures is 500 nm.

Third, we performed low-temperature annealing experiments to enhance impurity segregation in Cu-mixed nnt-Ag. Strikingly, the hardness value of nnt-Ag can be further increased from 2.76±0.16 GPa to 3.05±0.18 GPa at 423 K annealing conditions – a 11% increase over already-impressive hardness values. The 3.05±0.18 GPa value is ~42% above those reported in the literature for nt-Ag (the previous record value is ~2.15 GPa) [4] and surpasses the maximum strength observed in nt-Cu (~2.7 GPa) [11]. Our cross-section focused-ion-beam (FIB) and surface atomic force microscopy (AFM) studies of the as-deposited and 423K-annealed nnt-Ag samples indicate that annealing does not appreciably change d and λ of segregated materials (Figure 6), confirming that the additional hike in hardness (~11%) is not due to further refinement of microstructure but rather from impurity segregations.

We further investigate the electrical resistivity (ρ) of Ag nanostructures, as they are of potential interest for applications as transparent electrodes, catalysts, and plasmonic materials [12, 13]. Figure 7 compares the temperature-dependent ρ behavior for the pure nt-Ag, Cu-mixed nnt-Ag, Ag nanowire (227 nm in diameter) [3], bulk Ag [3], and nc-Cu [14] as a reference.
Figure 7: A. The electrical resistivity of nnt-Ag-0.81wt.% Cu between 4 and 300 K, in comparison with that of pure nt-Ag, nanocrystalline Cu (nc-Cu), Ag nanowire (227 nm in diameter), and bulk Ag. B. A summary of yield strength/shear modulus ($\sigma_y/\mu$) versus electrical conductivity of various metals and alloys, including nnt-Ag (our work), pure nt-metals, nanostructured Cu (nano-Cu), nano-Cu-alloys, ufg-Al, nano-Al, nano-Al-alloys, Cu-ceramics composites, and conventional commercial Cu alloys. The exceptional combination of strength and electrical conductivity in nnt-Ag exceeds that of existing materials, including the current benchmark nt-metals. The solid red line is a guide for the eye only.
At room temperature, the $\rho$ values for nt-Ag, 0.81 wt.% Cu-mixed nnt-Ag, Ag nanowire and nc-Cu are $1.80 \times 10^{-8}$ (\(\Omega\cdot\text{m}\)), $2.69 \times 10^{-8}$ (\(\Omega\cdot\text{m}\)), $7.78 \times 10^{-8}$ (\(\Omega\cdot\text{m}\)), and $1.90 \times 10^{-7}$ (\(\Omega\cdot\text{m}\)), respectively. The $\rho$ value of Cu-mixed nnt-Ag is three and seven times lower than that of Ag nanowire and nc-Cu (d ~ 15 nm), respectively, and is only marginally higher than that of pure nt-Ag. The electron mean free paths due to the structural defect scattering at 0 K for nt-Ag and 0.81 wt.% Cu-mixed nnt-Ag are estimated to be 33 and 8 nm, respectively. These values are larger than the $\lambda$ measured in both types of materials, indicative that TBs are not the dominant scattering sources for electrons. Thermal annealing of Cu-mixed nnt-Ag at 423 K is found to further reduce the electrical resistivity by $\sim 10\%$, and increases the electron mean free path by 12.5%. As the intrinsic strength of metals and alloys is linked to their shear modulus ($\mu$) [15], we normalize the yield strength ($\sigma_y$, hardness divided by 3) of Cu-mixed nnt-Ag by $\mu$ for fair comparison with the literature data. Interestingly, Figure 4 (b) indicates that the $\sigma_y/\mu$ values of our nnt-Ag well surpasses those reported in various nanostructured (nano) metals and alloys with similar electrical conductivities. This leads to an exceptional combination of strength and electrical conductivity that is far outside the inversely correlated strength-electrical conductivity zone typically seen in conventional commercial alloys and high-strength nano metals and alloys such as nano-Cu [16], nano-Cu-alloys [16], Cu-ceramics composites [17], ufg-Al [18], nano-Al [16], and nano-Al-alloys [16]. Notably, the performance of nnt-Ag extends even beyond the current benchmark pure nt-metals (i.e., nt-Cu and nt-Ag), signaling that our materials are of technological importance.
B. Solid solution strengthening theoretical estimate in Cu-mixed nt-Ag

Assuming both solid solution and GB hardening contribute to the hardness, and they are independent, therefore:

\[ H = H_0 + \Delta H_{SS} + \Delta H_{gb} \]  \hspace{1cm} (1)

where \( H_0 \) is the hardness caused by the friction stresses to move dislocations. \( \Delta H_{SS} \) is the increment of hardness resulting from solid-solution strengthening, and \( \Delta H_{gb} \) is the additional hardness due to grain refinement. Using a standard model for substitutional solid solution strengthening based on elastic dislocation interactions (Fleischer model) [19],

\[ \Delta H_{ss} = 3^{3/2} \frac{G \varepsilon_s^{3/2} \cdot c^{1/2}}{700} \]  \hspace{1cm} (2)

where \( G \) is the shear modulus of Ag, \( c \) is the atomic concentration of Cu, and the factor of \( 3^{3/2} \) has been introduced as an approximate conversion from shear stress to hardness. The \( \varepsilon_s \) is calculated from

\[ \varepsilon_s = \left| \frac{\varepsilon_G}{1 + \frac{1}{2} |\varepsilon_G|} \right| - 3 \varepsilon_s \]  \hspace{1cm} (3)

where the mismatch parameters are defined as:

\[ \varepsilon_G = \frac{1}{G} \frac{\partial G}{\partial c} \]  \hspace{1cm} (4)
\[ \varepsilon_a = \frac{1}{a} \frac{\partial a}{\partial c} \]  

where \( a \) is the lattice constant of Ag. Here we assume that both the lattice constant and shear modulus change linearly with the composition. At \( c = 0.81 \text{ wt.\%} \) or 1.37 at.\%, \( \varepsilon_G = 0.60, \varepsilon_a = -0.115, \varepsilon_s = 0.81, \Delta H_{ss} = 19 \text{ MPa} \). This value is negligible and consistent with our atomistic simulations. Similarly, according to a recent solute pinning model [19], the solute atoms can affect the global properties of lattice, which gives an argumentation of the hardness by

\[ \Delta H_{ss} = 3^{3/2} \frac{d_b}{d} \varepsilon_{cu} \cdot C_{cu} \]  

where \( d \) is the grain size, \( b \) is the Burger’s vector of Ag, and \( \varepsilon_{cu} \) is given by

\[ \varepsilon_{cu} = \frac{1}{g} \frac{\partial G}{\partial c} + \frac{1}{b} \frac{\partial b}{\partial c} \]  

Equation 6 yields an estimated \( \Delta H = 8 \text{ MPa} \). This value is again negligibly small. Table 2 presents the parameters used to obtain the above estimate.

<table>
<thead>
<tr>
<th>Material</th>
<th>Shear modulus ( G ) (GPa)</th>
<th>Lattice constant ( a ) (nm)</th>
<th>Burgers vector ( b ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>30</td>
<td>0.409</td>
<td>0.289</td>
</tr>
<tr>
<td>Cu</td>
<td>48</td>
<td>0.362</td>
<td>0.256</td>
</tr>
</tbody>
</table>
C. Continuum Model for TB-defect Softening

The softening behavior of defective nt materials is identified to be caused by the motion or splitting of TB kink steps, which is particularly pervasive at $\lambda = 1.4$ nm, Figure 3.9 (b). We have developed a continuum theory predicting the softening behavior from kink motion.

This model is based on the following assumptions derived from our MD simulations.

1. The geometry of a representative grain is that given in Figure 8. The grain size, $d$, is constant, but the TB spacing, $\lambda$, can be varied.

2. The material has already reached its Hall-Petch limit, where deformation is predominantly carried out by GB plasticity controlled by the local GB stress, and independent on $\lambda$.

3. Below some critical $\lambda_T$, kinks are no longer stable, and deformation is carried out via kink motion on coherent TBs, by either kink-step migration or splitting parallel to the TB plane [20].

![Figure 8: Schematic diagram of a crystal grain of cubic shape and size d, with internal twin spacing $\lambda$ used for the kink-softening model.](image)
During deformation by the motion of an existing density of kinks, the slip rate is:

$$\dot{\gamma}_k = \rho_k h \nu_k$$  \hspace{1cm} (8)

where $\rho_k$ is the prescribed kink density (in units of $[m^{-2}]$), $h$ is the kink step height, and $\nu_k$ is the kink velocity. The kink velocity is typically a linear function of the stress:

$$\nu_k = \frac{h(\sigma - \sigma^\ast)}{B}$$  \hspace{1cm} (9)

where $\sigma^\ast$ is a threshold stress and $B$ is a friction coefficient. If there are $n$ kinks on each coherent TB interface, the total number of kinks in a grain is $n(d/\lambda)$, where the term in parenthesis represents the number of TBs in a grain. Because each kink has an effective length of $d$ (they traverse the entire grain), the kink density $\rho_k$ is:

$$\rho_k = n \left( \frac{d}{\lambda} \right) \left( \frac{d}{d} \right) = \frac{n}{\lambda d} = \frac{\alpha}{\lambda}$$  \hspace{1cm} (10)

where $\alpha = n/d$ is the average number of kink steps per units of TB length ($\alpha = 1/10$ kink/nm in our MD simulations). Inserting Equations 4 and 5 into Equation 3, one gets:

$$\dot{\gamma}_k = \frac{\alpha h^2}{\lambda B} (\sigma - \sigma^\ast)$$  \hspace{1cm} (11)

which has units of $[s^{-1}]$ when $B$ is expressed in $[Pa \cdot s]$. 

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The transition from GB-stress controlled regime to kink-motion softening will occur when both deformation rates are equal, i.e.:

\[ \dot{\gamma}_k \approx \dot{\gamma}_{GB} \]  

where \( \dot{\gamma}_{GB} \) is the maximum GB deformation rate obtained from Figure 3.3 (f).

This equality can be arranged, solving for the stress, in which case:

\[ \sigma = \sigma^* + \left( \frac{\dot{\gamma}_{GB} B}{\alpha h^2} \right) \lambda \]  

Application to MD simulation results:

The parameters of the kink-motion softening theory as applied to pure and Cu-segregated nnt-Ag atomistic models, are shown in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pure nnt-Ag</th>
<th>Cu-segregated nnt-Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical stress ( \sigma^* ) (GPa)</td>
<td>1.23</td>
<td>1.39</td>
</tr>
<tr>
<td>Friction coefficient B (GPa·ps)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>GB deformation rate from Figure 3.3 (f) (ps(^{-1}))</td>
<td>0.0011</td>
<td>0.0015</td>
</tr>
<tr>
<td>Kink number ( \alpha ) (nm(^{-1}))</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Kink height ( h ) (nm)</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Equation 10 is used directly without fitting to obtain the theoretical kink density as a function of $\lambda$, Figure 3.9 (c). We find an excellent agreement between theoretical kink density and density of Shockley partial dislocation in our MD models with kinked TBs for $\lambda \leq 3.5$ nm. This is because a kink step is made by stacking three (111)<112> partial dislocations with Burgers vector parallel to the TB plane, and kink deformation proceeds by migration of Shockley partial dislocations. For larger $\lambda$ values, however, the kink density becomes significantly smaller than the density of partial dislocations due to GB-mediated dislocation emission. As a result, the dislocation density difference between models with either perfect or kinked TBs becomes negligible for $\lambda \geq 10$ nm.

The flow stress from Equation 13 is represented in Figure 3.9 (d). For the parameters in this equation, it was assumed that (1) the friction coefficient B does not change with Cu segregation, because it was shown that solid solution strengthening from impurities was absent in our MD simulations, and (2) the critical stress $\sigma^*$ and B are considered as fitting parameters. Figure 3.9 (d) shows good agreement between plastic flow stresses from kink-motion softening theory and MD predictions. We find the same transition $\lambda_T = 2.8$ nm for both pure and Cu-segregated models.

Because each kink has an effective length of $d$ (they extend through the entire grain), the density of kink steps in motion $\rho_k$ can be estimated as:

$$\rho_k = \frac{\alpha}{\lambda} \quad (14)$$
where $\alpha$ is the average number of kink steps per unit of TB length. Here, we fixed $\alpha = 1/10 \text{ kink/nm}$ in our MD simulations based on the previous experimental observations [21]. Figure 3.9 (c) demonstrates that the theoretical kink density dominates the density of Shockley dislocations that can actively participate in plastic deformation, when $\lambda \leq 3.5 \text{ nm}$. Our continuum model shows that the softening stress associated with kink motion can be expressed as

$$\sigma = \sigma^* + \left( \frac{\dot{\gamma}_{GB} B}{\alpha h^2} \right) \lambda$$

(15)

where $\sigma^*$ is a threshold stress, $B$ is a friction coefficient, $h$ is the height of a kink step, and $\dot{\gamma}_{GB}$ is the maximum GB shear-strain rate. MD predictions and the proposed theory from Equation 15 show excellent agreement when $\lambda \leq 2.8 \text{ nm}$, Figure 3.9 (d). This defect-induced softening is consistent with the original experimental report in nt-Cu [11].

**D. Ab initio Calculations of Segregation Energies**

Calculations of segregation enthalpies for solute Cu atoms in (112) twin-boundary kink steps and $\Sigma 9$ (221) grain-boundary in Ag were performed using the Vienna Ab initio simulation package (VASP). Gamma point geometry optimization was used to obtain the minimum potential energy of each single-crystal, kink, and GB configurations without and with Cu impurity at specific sites. We used plane wave basis sets to expand Kohn-Sham orbitals with a cutoff energy of 350 eV, and the
exchange-correlation functional based on generalized gradient approximation scheme [22]. Interaction between ions and electrons was modeled using the projector augmented wavefunction method pseudopotentials. The convergence criterion is $10^{-6}$ eV for wave function optimization and $10^{-4}$ eV/Å for geometry optimization. The atomistic models used for kink steps and high energy GB are shown in Figure 9, along with the number of each atomic sites used to compute the different segregation enthalpies. The ab-initio calculations were all performed on the NERSC’s Cori supercomputer.

Figure 9: Simulation cells used in VASP DFT-based ab-initio calculations of Cu solute segregation enthalpies for different segregation sites in A. a (112) kink TB step defect and B. a high-angle symmetric [110] tilt GB. The models have periodic boundary conditions.
Figure 10: Structure of an internal twin-boundary kink-step defect with first-principles density-functional-theory calculations of the six highest substitutional segregation energies from different local sites of a twin-boundary kink step and a high-energy \( \Sigma^9 \) (211) tilt grain boundary, respectively. Sites 1-6 of the kink defect are indicated.

E. Acknowledgements

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AC at Los Alamos National Laboratory are supported under DOE Contract DE-AC52-06NA253. YMW and DXQ acknowledge the support of LDRD program (17-ERD-048) at LLNL. JM acknowledges support from the National Science Foundation (NSF) grant DMR-1611342. The simulations in this research used resources of the National Energy Research Scientific Computing Centre, supported by DOE Contract DE-AC02-05CH11231, and those of the Extreme Science and Engineering Discovery Environment, supported by NSF grant ACI-1548562. Author Contributions: YMW and FS conceived and guided the research. JCY, MB, LF, JG, RTO, and YMW performed the synthesis, mechanical testing, and characterizations. DXQ performed the electrical measurements. AC developed the initial MC/MD code. XK and FS performed the MC/MD simulations and atomistic analysis. ZP performed the DFT calculations. JM and FS developed the continuum softening model. All authors contributed to the data discussion and manuscript preparation. Competing interests: The authors have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials.

E. Reference


2. LAMMPS Script for MC/MD Simulations

# LAMMPS version: 10Feb15

units          metal
atom_style     atomic
boundary        p p p
newton          on
variable       t equal 500.0
read_data      Data.in.gz
set            group all type/fraction 2 1.0 43534
pair_style     eam/alloy
pair_coeff      * * cu_ag_ymwu.eam.alloy Cu Ag
fix             integrate all nve
thermo_modify   flush yes
thermo          100
#min_style      cg
#minimize       1.0e-10 1.0e-12 1000 10000
velocity       all create $t 4928459 rot yes dist gaussian
timestep       0.002
compute        potene all pe/atom
fix             T_control all temp/rescale 10 $t $t 5. 1
fix             press_ctrl all press/berendsen aniso 0.0 0.0 1000.0
fix           mc all sgcmc 100000 1 $t -2.5  randseed 324234 variance 100 0.940

window_moves 8

f_mc[4]

run 1000

dump          2 all custom 500 frames-3Cu.dat.* x y z type c_potene

restart       500 restart.dat

unfix         mc

#fix          T_control all temp/rescale 10 500. 500. 5. 1

fix          mc all sgcmc 10 1 $t -2.5  randseed 324234 variance 100 0.940

window_moves 8

f_mc[4]

run          1000000
Bash script “script_run” for submit jobs on supercomputers

#!/bin/bash

#PBS -q workq
#PBS -A TG-DMR130119
#PBS -l nodes=35:ppn=20,walltime=12:00:00
#PBS -N grs45-kink14-tension
#PBS -j oe
#PBS -M xke@uvm.edu
#PBS -m bea

echo "This is in.tension-restart2 being started..."

cd /work/xke/gr45-kink14-tension

mpirun -np 700 -machinefile $PBS_NODEFILE ~/lammps-10Feb15/src/lmp_intel_phi
-in /work/xke/gr45-kink14-tension/in.tensionxx-restart2
3. LAMMPS Script for Tension Simulation

```
echo both
read_restart restart.dat

#EAM
pair_style eam/alloy
pair_coeff * * cu_ag_ymwu.eam.alloy Cu Ag
timestep 0.005
compute ctr all cna/atom 3.491
compute str all stress/atom NULL
#compute pe all pe/atom

# Equilibration from 500k to 300k under zero stress
thermo_style one
thermo 1000
dump 11 all custom 10000 coord0.xyz xs ys zs id type
fix 16 all npt temp 500 300 0.05 aniso 0.0 0.0 0.12 drag 2
run 20000
unfix 16
undump 11

# Equilibration at 300K under zero stress
thermo_style one
thermo 1000
```
dump       10 all custom 10000 coord0.xyz xs ys zs id type
fix        15 all npt temp 300 300 0.05 aniso 0.0 0.0 0.12 drag 2
run        20000
unfix      15
undump     10
#Deformation simulation
restart    50000 restart
reset_timestep  0
fix        25 all deform 1 x erate 0.0001
fix        35 all npt temp 300.0 300.0 0.05 y 0.0 0.0 0.12 z 0.0 0.0 0.12 drag 2
variable a loop 20
label     repeat20
dump      45 all custom 1000 coord$a$.xyz xs ys zs id type c_ctr c_str[1]
run       10000
undump    45
next       a
jump      in.tensionxx-restart2 repeat20
4. Python Script for Identification of a Three-dimensional GB Network

File one: “cid.py”

#Python version: 2.7.13; Numpy version: 1.11.3

# Dump the structures of coordF with only GB

# Run “cid.py”, “voronoi_functions.py”, “voronoi_centers_data_file”, and

“coordF*.dump.gz” files under the same folder

import numpy as np

import voronoi_functions

from scipy.spatial import Voronoi

import time

import gzip

import os.path

float_formatter = lambda x: "%5.2f" % x

np.set_printoptions(threshold=np.nan, precision=3, formatter={"float_kind":float_formatter})


def main():
    # Half of GB wall thickness

    gb_thickness = 4.72

    # Half of simulation box size

    simu_box = 240
### CID list create and dump

coordxyz_001 = np.loadtxt('coordF001.dump.gz', skiprows=9)

tf_list_c_id = voronoi_functions.get_tf_list("coordF001.dump.gz", coordxyz_001, gb_thickness, simu_box)

np.savetxt('cid.gz', tf_list_c_id)

### GB dump

total_atom, x_size, y_size, z_size, pb_box = voronoi_functions.read_file_header('coordF001.dump.gz')

coordxyz_reduced = np.delete(coordxyz_001, np.where(tf_list_c_id >= 0), axis=0)

total_c_atom = np.shape(coordxyz_reduced)[0]

voronoi_functions.file_dumping(total_c_atom, 'coordF_001_gb.dump.gz', coordxyz_reduced, pb_box)

del coordxyz_001

del coordxyz_reduced

if __name__ == '__main__':
    main()

# References

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import numpy as np

from scipy.spatial import Voronoi

import time

import gzip

import os.path

float_formatter = lambda x: "%.5f" % x

np.set_printoptions(threshold=np.nan, precision=3, formatter={'float_kind':float_formatter})

start_time = time.time()

def read_file_header(file_name):
    if os.path.isfile(file_name):
        header_rows = 9
        with gzip.open(file_name) as f:
            for i in range(header_rows):
                exec ('line%d = f.readline()' % i)
        total_atom = int(line3)
        x_min, x_max = float(line5.split()[0]), float(line5.split()[1])
        y_min, y_max = float(line6.split()[0]), float(line6.split()[1])
        z_min, z_max = float(line7.split()[0]), float(line7.split()[1])
        pb_box = np.array([[x_min, x_max], [y_min, y_max], [z_min, z_max]])
        x_size = float(line5.split()[1]) - float(line5.split()[0])

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y_size = float(line6.split()[1]) - float(line6.split()[0])

z_size = float(line7.split()[1]) - float(line7.split()[0])

print file_name + ' header read, %d atoms with x = %f A, y = %f A, z = %f A' % (total_atom, x_size, y_size, z_size)

else:
    print file_name + ' not found, skipped header reading.'

return total_atom, x_size, y_size, z_size, pb_box

def voronoi_prep(file_name,x_size,y_size,z_size,simu_box):

    # input file name
    # output rescaled voronoi centers and related coordinates
    vcenters = np.delete(np.loadtxt(file_name),0,axis=1)

    pb_size_0 = simu_box

    vcenters[:,0] = vcenters[:,0]*x_size/(2*pb_size_0)
    vcenters[:,1] = vcenters[:,1]*y_size/(2*pb_size_0)
    vcenters[:,2] = vcenters[:,2]*z_size/(2*pb_size_0)

    vcenters_expand = np.empty((0,3))
    vcenters_expand_mask = np.empty((0,3))

    c_id = np.arange(np.shape(vcenters)[0])
    c_id_expand = np.empty(0)

    for i in range(-1,2):
        for j in range(-1,2):
            ...
for k in range(-1,2):
    temp = vcenters-np.array([[x_size*i,y_size*j,z_size*k]])
    vcenters_expand = np.append(vcenters_expand,temp,axis=0)
    vcenters_expand_mask = np.append(vcenters_expand_mask,vcenters,axis=0)
    c_id_expand = np.append(c_id_expand,c_id)
return vcenters, vcenters_expand,vcenters_expand_mask,c_id,c_id_expand

def voronoi_centers_inbox_index(pb_enlarge_factor,pb_box_in,vor_points):
    # define box for calculating centers
    print 'This simulation use pb-enlarge-factor %f'%pb_enlarge_factor
    pb_box_en = pb_box_in * pb_enlarge_factor
    center_inbox = np.empty(0,dtype=int)
    for ve in range(np.shape(vor_points)[0]):
        if vor_points[ve,0] > pb_box_en[0,0] and vor_points[ve,0] < pb_box_en[0,1] \
        and vor_points[ve,1] > pb_box_en[1,0] and vor_points[ve,1] < pb_box_en[1,1] \
        and vor_points[ve,2] > pb_box_en[2,0] and vor_points[ve,2] < pb_box_en[2,1]:
            center_inbox = np.append(center_inbox, ve)
    return center_inbox

def voronoi_nb_index(vor_id,vor_ridge_points):
    # input index of a center
    # output its neighbour list

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nb_index = np.empty(0)
for rp in vor_ridge_points:
    if rp[0] == vor_id:
        nb_index = np.append(nb_index, rp[1])
    elif rp[1] == vor_id:
        nb_index = np.append(nb_index, rp[0])
return nb_index

def voronoi_centers_out_box_index(centers_inbox_index, vor_ridge_points):
    # input centers_inbox_index
    # output its surrounding neighbours
    centers_nb_index = np.empty(0)
    for i in centers_inbox_index:
        for j in voronoi_nb_index(i, vor_ridge_points):
            if j in centers_inbox_index:
                pass
            else:
                centers_nb_index = np.append(centers_nb_index, j)
    return np.unique(centers_nb_index)

def voronoi_crys_id(index_list, crystallite_id, vcenters_expand_mask, vcenters):
    # input: a list of centers
# output: its original crystallite number list

index_list_cid = np.empty(0)

for i in index_list:
    for j in crystallite_id:
        if np.array_equal(vcenters_expand_mask[i, :], vcenters[j, :]):
            index_list_cid = np.append(index_list_cid, j)

if np.shape(index_list) != np.shape(index_list_cid):
    print 'ERROR: missing centers in voronoi_crys_id()'

return index_list_cid

def proj_eval(center_id, gb_thickness, total_atom, vor_ridge_points, vor_points, coordxyz):

    # input: a center

    # output: T/F list for the center, T for crystallite atom

tf_list = np.ones(total_atom) > 0

    for i in voronoi_nb_index(center_id, vor_ridge_points):
        vector_proj = vor_points[i, :] - vor_points[center_id, :]

        evaluator = (np.linalg.norm(vector_proj)/2 - gb_thickness)*np.linalg.norm(vector_proj)

        tf_list = np.logical_and(tf_list, np.inner(coordxyz - vor_points[center_id, :], vector_proj).flatten() <= evaluator)

    return tf_list
def crys_regroup(ID, vor_inbox_index, vor_outbox_nb_index, vor_inbox_index_cid, vor_outbox_nb_index_cid):
    # input ID of the crystallite
    # return list of all crystallites
    merged_center_index = np.append(vor_inbox_index, vor_outbox_nb_index)
    merged_center_mask = np.append(vor_inbox_index_cid, vor_outbox_nb_index_cid)
    c_grouped = np.empty(0)
    c_grouped = np.append(c_grouped, merged_center_index[merged_center_mask == ID])
    return c_grouped

def get_tf_list(file_name, coordxyz, gb_thickness, simu_box):
    total_atom, x_size, y_size, z_size, pb_box = read_file_header(file_name)
    vcenters, vcenters_expand, vcenters_expand_mask, crystallite_id, crystallite_id_expand = voronoi_prep('voronoi-centers-45grs.txt', x_size, y_size, z_size, simu_box)
    vor = Voronoi(vcenters_expand)
    vor_inbox_index = voronoi_centers_inbox_index(1.5, pb_box, vor.points)
    vor_outbox_nb_index = voronoi_centers_out_box_index(vor_inbox_index, vor.ridge_points)
vor_inbox_index_cid = voronoi_crys_id(vor_inbox_index, crystallite_id, vcenters_expand_mask, vcenters)

vor_outbox_nb_index_cid = voronoi_crys_id(vor_outbox_nb_index, crystallite_id, vcenters_expand_mask, vcenters)

tf_list_c_id = np.ones(total_atom) * (-1)

for g_i in range(np.shape(vcenters)[0]):
    tf_list = np.ones(total_atom) < 0

    for g_j in crys_regroup(g_i, vor_inbox_index, vor_outbox_nb_index, vor_inbox_index_cid, vor_outbox_nb_index_cid):
        tf_list = np.logical_or(tf_list, proj_eval(g_j, gb_thickness, total_atom, vor.ridge_points, vor.points, coordxyz))

    tf_list_c_id[np.where(tf_list == True)] = g_i

return tf_list_c_id

def file_dumping(total_c_atom, file_name_in, coordxyz_c, pb_box):
    header = "

    header_rows = 9

    line0 = 'ITEM: TIMESTEP\n'
    line1 = '0\n'
    line2 = 'ITEM: NUMBER OF ATOMS\n'
    line3 = '%d\n' % total_c_atom
    line4 = 'ITEM: BOX BOUNDS\n'
line5 = '%6.2f %6.2f\n' % (pb_box[0, 0], pb_box[0, 1])
line6 = '%6.2f %6.2f\n' % (pb_box[1, 0], pb_box[1, 1])
line7 = '%6.2f %6.2f\n' % (pb_box[2, 0], pb_box[2, 1])

line8 = 'ITEM: ATOMS x y z'

for i in range(header_rows):
    exec ('header += line%d' % i)
else:
    "Files not found for %s"%file_name_in

file_name_out = file_name_in[:9] + '_no_gb' + file_name_in[9:]
np.savetxt(file_name_out, coordxyz_c,header=header.strip(),fmt='%10.2f',comments='')