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Stabilization and strengthening of nanocrystalline copper by alloying with tantalum

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Received 10 June 2011; received in revised form 29 December 2011; accepted 8 January 2012

Abstract

Nanocrystalline Cu–Ta alloys belong to an emerging class of immiscible high-strength materials with a significant potential for high-temperature applications. Using molecular dynamics simulations with an angular-dependent interatomic potential, we study the effect of Ta on the resistance to grain growth and mechanical strength of nanocrystalline Cu–6.5 at.% Ta alloys. Ta segregation at grain boundaries greatly increases structural stability and strength in comparison with pure copper and alloys with a uniform distribution of the same amount of Ta. At high temperatures, the segregated Ta atoms agglomerate and form a set of nanoclusters located at grain boundaries. These nanoclusters are capable of pinning grain boundaries and effectively preventing grain growth. It is suggested that the nanoclusters are precursors to the formation of larger Ta particles found in Cu–Ta alloys experimentally.

Keywords: Nanocrystalline materials; Molecular dynamics; Segregation; Grain growth

1. Introduction

Alloying with immiscible elements is a promising approach to the design of materials with extraordinary structural stability and mechanical strength at high temperatures [1–5]. Immiscible elements tend to strongly segregate to grain boundaries (GBs), reducing their free energy and thus the capillary driving force for grain growth. They can also reduce GB mobility through the solute drag effect. In addition, immiscible elements often form highly dispersed particles that effectively pin GBs and create strong obstacles to dislocation motion. These effects can be especially important in nanocrystalline materials, whose limited thermal stability is one of the impediments to high-temperature applications.

Cu–Ta is an example of an immiscible system presenting a significant technological interest. The pure elements of this system have different crystalline structures and negligible mutual solubility in the solid state. The melting temperatures of Cu and Ta are also very different: 1356 and 3290 K, respectively. The experimental phase diagram of the Cu–Ta system contains a σ-shape liquidus connecting the melting points of the pure elements [6]. The nearly flat region of the liquidus suggests the existence of a metastable liquid–liquid miscibility gap at lower temperatures. A metastable Cu-rich solid solution can accommodate up to 10–20 at.% Ta, with higher concentrations causing amorphization [7–11]. In nano- and microelectronic applications, Ta thin films can be used as diffusion barriers separating Cu conductor lines from the semiconductor substrate [12–15]. Thus, interaction of a Ta surface with copper is relevant to fabrication of electronic devices and was investigated in recent experimental and computational studies [10,11,16–19].

Several processing methods have been applied to produce bulk Cu–Ta alloys with 5 or more at.% Ta, including ball milling, ion beam mixing and physical vapor deposition (see Ref. [4] for a review). The initial structure of the alloy typically contains body-centered cubic (bcc) Ta
particles a few nanometers in diameter randomly dispersed in nanocrystalline face-centered cubic (fcc) Cu. Such alloys demonstrate a drastically improved thermal stability (resistance to grain growth at elevated temperatures) in comparison with other Cu-based alloys. For example, no substantial structural changes were found in Cu–Ta alloys with 2–20 nm Ta particles and 200 nm Cu grains annealed for 10 h at 1173 K, suggesting that the GBs were strongly pinned by the Ta particles [4].

Further understanding as well as improvements in thermal stability and strength of nanocrystalline Cu–Ta alloys require efforts not only in processing, fabrication and characterization but also in computer modeling and simulation. We are not aware of previous simulation work on thermal and mechanical behavior of nanocrystalline Cu–Ta alloys. Thus the atomistic simulations reported in this paper appear to mark the first step in this direction.

As a motivation for our simulation study, Fig. 1 presents some preliminary results of a concurrent experimental work. A Cu–10 at.% Ta alloy was produced by ball milling with a structure composed of Cu and Ta grains less than 10 nm in diameter. The hardness of this alloy was found to be nearly twice the hardness of nanocrystalline copper with a comparable grain size. More importantly, while nanocrystalline copper drastically softens with temperature due to rapid grain growth, the ball-milled Cu–Ta alloy suffers only a moderate reduction in hardness and remains extraordinarily hard even the temperature of 1173 K (0.87 of the melting point of Cu). At this high temperature, a 4 h long anneal results in copper grains of about 111 nm in diameter and Ta particles with a very broad distribution of sizes (Fig. 1a). The average size of the Ta particles is about 49 nm. However, a magnified image of the structure reveals the presence of much smaller particles residing at the copper GBs (Fig. 1b). An even higher magnification reveals particles as small as 7 nm and less (Fig. 1c).

To understand the origin of the Ta nanoparticles at GBs and their role in thermal stability and strength of Cu–Ta alloys, we have launched a systematic atomistic simulation study of structural evolution in such alloys at elevated temperatures. In this paper we present the initial results of the study, focusing on the role of Ta segregation and its possible relation to the growth of Ta nanoparticles. After introducing our simulation methodology in Section 2, we report on structural evolution in Cu–Ta alloys at different temperatures (Section 3) and the effect of Ta on mechanical strength of the alloys (Section 4). To facilitate the interpretation of the results, we performed calculations of diffusion coefficients and segregation energies in a representative GB in Cu, which are reported in Sections 5 and 6, respectively. Our findings are summarized and discussed in Section 7.

2. Methodology of atomistic simulations

Interactions between atoms in the binary Cu–Ta system were modeled with the angular-dependent interatomic potential fit to experimental data and first-principles calculations [17]. The potential was constructed by crossing previously developed elemental potentials for Cu [20] and Ta [21]. The melting temperatures of the pure elements predicted by this potentials are $T_{\text{Cu}}^{m} = 1327$ K for copper and $T_{\text{Ta}}^{m} = 3960$ K for tantalum. In agreement with the experimental phase diagram [6], the potential reproduces nearly zero mutual solubility between the solid phases. Molecular dynamics (MD) simulations were performed with the ITAP Molecular Dynamics (IMD) code [22] with temperature controlled by a Nose–Hoover thermostat. We used the
NPT ensemble implemented in the IMD code to perform stress-free simulations and the tensile tests as explained below. The GB diffusion simulations employed the NVT ensemble with certain restrictions imposed on the motion of surface atoms, as explained below.

The simulation block used to model a nanocrystal had the dimensions $11 \times 15 \times 10 \text{ nm}^3$, included 112,320 atoms and had periodic boundary conditions in all directions. It initially contained only copper atoms and had a polycrystalline structure with grain diameters ranging from $\sim1$ to $\sim5$ nm. Besides general GBs and triple junctions, the structure contained twin boundaries, stacking faults and dislocations. The initially created structure was partially relaxed by a 1 ns MD run at the temperature of 100 K and zero pressure. We emphasize that the polycrystalline structure was deliberately equilibrated only partially as it was designed to mimic the highly non-equilibrium experimental microstructures produced by ball milling.

High-energy ball milling experiments have the potential to dramatically force Ta into polycrystalline Cu. Given the negligible equilibrium solubility of Ta in Cu, it is expected that during the subsequent heat treatments most of the Ta atoms end up at GBs. To model such ball-milled alloys in the computer, $c_0 = 6.5$ at.% of copper atoms were replaced by Ta. Two different distributions of Ta atoms were created: (i) uniform random distribution and (ii) Ta segregation at GBs and other crystalline defects. The uniform distribution was simply obtained by atomic substitution using a random numbers generator. To prepare a segregated sample, we first selected copper atoms that were most likely to be located at GBs, in dislocation core regions and in other defects. Such atoms were identified by a characteristically high potential energy and comprised approximately 23.5% of all atoms. Then 28% of such high-energy atoms (and only of such atoms) were randomly substituted by Ta until the average alloy composition reached $c_0$. This procedure produced a structure with GBs and other defects decorated with Ta atoms. If we assume that all Ta atoms are located at GBs and approximate the GB thickness by two monolayers, the created Ta segregation is equivalent to 0.56 of a monolayer. This estimate is an upper bound of GB segregation because some of the Ta atoms decorate dislocations and stacking faults inside the grains. Once the uniform and segregated Cu–Ta alloys were obtained, they were re-annealed for 2 ns at 100 K and zero pressure to allow partial relaxation.

To evaluate the thermal stability of the obtained structures, they were subject to two types of thermal treatment. In one, temperature of the sample was steadily increased from 100 K to $T_m$ in 10 ns for pure Cu and in 1 ns for Cu–Ta alloys. In the other, the sample was gradually heated to a desired temperature and then subject to an isothermal anneal. In both cases, numerous snapshots containing atomic coordinates, energies and stresses were saved during the simulations. These snapshots were later used to examine the structural changes during the heatings and isothermal anneals as functions of time. A suitable quantitative measure of coarsening of the structure would be the average grain size. However, due to the limited number of grains in the sample and the presence of twins and other defects, it was impossible to gather sufficient statistics for calculations of grain size distributions and average grain sizes. Therefore, we resorted to a more indirect measure of structure coarsening.

Specifically, the set of atomic coordinates saved in every snapshot was subject to the common neighbor analysis (CNA) [23] implemented in one of the utilities of the IMD code [22]. The CNA algorithm identifies atoms with a nearly perfect fcc environment and atoms with a hexagonal close-packed (hcp) environment. The former occupy relatively undistorted regions inside the grains while the latter are typically located at stacking faults. Atoms not identified as fcc or hcp are predominantly located in GBs and other defects. Thus, the percentage of fcc atoms characterizes the degree of perfection of the structure and is expected to correlate with the average grain size. We will denote the percentage of fcc atoms by $\xi$ and refer to it as the “order parameter”. In a well-annealed single-crystalline material $\xi$ approaches 100%. Although not a direct quantitative measure of the grain size, this order parameter provides a useful metric for comparison of coarsening kinetics in different samples.

Two different visualization methods were used for qualitative examination of the structures. One method is based on the centrosymmetry parameter $P$ [24] implemented in the AtomEye visualization package [25]. The centrosymmetry parameter identifies atoms with broken cubic symmetry, which usually correlate with defect cores. Atoms residing inside the grains have a nearly perfect fcc environment and their $P$ is close to zero. In the images shown in this paper, such atoms appear dark blue. Atoms located in GBs and other defects appear yellow (larger $P$) or red (even larger $P$). To demonstrate the distribution of Ta atoms in the structure, we use a different visualization method in which Ta atoms are shown as dark blue spheres while copper atoms as yellow spheres. In addition, Ta atoms are represented by larger spheres than Cu atoms to reflect the actual difference in atomic sizes.

To obtain a quantitative proof of Ta clustering observed in Cu–Ta alloys at high temperatures, the radial distribution function (RDF) of Ta–Ta pairs was computed using the relevant utility of the IMD code [22]. The RDF represents properly normalized numbers of Ta–Ta bonds with various radii averaged over the simulation block. Although RDFs were also computed for Cu–Cu and Cu–Ta pairs, only results for the Ta–Ta pairs are reported in this work.

To evaluate the effect of Ta alloying on mechanical properties of Cu, we performed simulated tensile tests at the temperature of 300 K. For pure copper, the sample relaxed at 100 K was heated to 300 K and subjected to the test. For the Cu–Ta alloys, the tests were performed on the final structures obtained after the isothermal anneals mentioned above (at the temperatures of 750, 1000 and
1100 K) and after they had been cooled down to 300 K. The tensile test was implemented in the NPT ensemble by scaling atomic coordinates to gradually increase the stress \( \sigma_{zz} \) in a chosen tensile direction \( z \) (parallel to one of the edges of the simulation block) while keeping \( \sigma_{xx} = \sigma_{yy} = 0 \). The applied tensile stress was ramped up at a constant rate of 0.15 GPa ns\(^{-1} \) under isothermal conditions. The MD snapshots saved during the test contained information about the block dimensions and allowed calculation of the finite strain

\[
e_{zz} = \ln \frac{L_z}{L_z^0},
\]

where \( L_z \) and \( L_z^0 \) are the \( z \) dimensions of the simulation block in the current state of stress and at zero stress, respectively.

It should be noted that the stress–strain curves obtained by the test could have been affected by the limited sample size, the high strain rate and other simulation constraints. Furthermore, the periodic boundary conditions do not allow the material to form a neck at late stages of deformation. Thus the stress–strain curves obtained here were not intended for making quantitative experimental predictions. They only served for a qualitative demonstration of the possible impact of Ta and its distribution in the structure on mechanical strength of the material.

To evaluate the diffusivity of Ta in Cu GBs, we chose the \( \Sigma 5 \) (210) symmetrical tilt boundary as a representative high-angle boundary in polycrystals. Although considered “special” in the sense of a small \( \Sigma \) value (reciprocal density of coincident sites) \[26\], previous simulation studies \[27–29\] have shown that this boundary is typical with respect to self-diffusion, perhaps closer to the higher end of the GB diffusivity spectrum. This GB was created in a simulation block with dimensions \( 5 \times 5 \times 20 \text{ nm} \) containing about 36,000 atoms. Periodic boundary conditions were imposed in the \( x \) and \( y \) directions parallel and normal to the tilt axis, respectively. In the \( z \) direction normal to the GB plane, the grains terminated at surfaces. Atoms within several crystal planes near each surface were allowed to move only in the \( z \) direction while their \( x \) and \( y \) coordinates were fixed. After the simulation block was equilibrated for 1 ns at the temperature of 1000 K, 10% of Cu atoms were randomly substituted by Ta and the block was re-equilibrated for 2 ns at the same temperature. The production runs for diffusion simulations were conducted at the temperatures of 1000, 1100 and 1200 K for 16.4, 10 and 10 ns, respectively. Snapshots containing the atomic coordinates were saved every 0.02 ns and later post-processed to compute the diffusion coefficients.

The methodology of diffusion calculations was similar to the one used in our recent study \[29\]. The GB diffusion coefficients \( D \) were extracted from linear fits of \( \langle x^2 \rangle \) vs. \( t \) plots using the Einstein relation \( D = \langle x^2 \rangle / 2t \). Here, \( t \) is the diffusion time and \( \langle x^2 \rangle \) is the mean-squared displacement of atoms over a time period \( t \) in the \( x \) direction parallel to the tilt axis. To compute \( \langle x^2 \rangle \), we used the initial and final coordinates of all atoms initially contained within a 10 Å thick probe layer centered at the boundary. The squared displacements of such atoms in the \( x \) direction were computed and linearized as functions of time over the interval between \( t \) and \( t + \Delta t \), where \( \Delta t \) was chosen to be 1 ns. The obtained diffusion coefficient was additionally averaged over all choices of the starting time \( t \) by increasing it from zero to \( t_{\text{max}} - \Delta t \), where \( t_{\text{max}} \) is the duration of the entire MD simulation. The latter averaging produced the reported values of the diffusion coefficients and their statistical error bars. Similar calculations were performed for diffusion in the \( y \) direction. Since no anisotropy of diffusivity was detected within the error bars of the calculations, the finally reported \( D \) values were obtained by averaging over both directions.

The described calculations were conducted separately for GB diffusion of Cu and Ta atoms, giving the coefficients of Cu self-diffusion and Ta solute diffusion, respectively. To evaluate the lattice diffusion, the above calculations were repeated for mean-squared atomic displacements within grain regions unperturbed by the presence of the GB or the surfaces. To evaluate the strength of Ta GB segregation in Cu, we used the same \( \Sigma 5 \) (210) boundary relaxed at 0 K. A single Ta atom was introduced in different substitutional positions in and around the GB core region as well as inside the grains. The segregation energy was computed as \( E_s = E_{\text{GB}} - E_{\text{g}} \), where \( E_{\text{GB}} \) and \( E_{\text{g}} \) are the relaxed total energies of the simulation block with the Ta atom at a given position in/near the GB core and with the Ta atom deep inside a grain beyond the influence of the GB or the surfaces. In addition, \( E_{\text{s}} \) was computed by placing Ta in the interstitial position at the center of the kink-shaped structural unit of the boundary. To preserve the total number of atoms, an isolated vacancy was simultaneously created in the GB core and placed in a position that minimized the total energy.

### 3. Results for structural stability

#### 3.1. Pure copper

When a pure copper sample was gradually heated from 100 K to \( T_m^\text{Cu} \), a noticeable grain growth started at about 500 K. At higher temperatures, extensive grain growth was observed until GBs completely disappeared, leaving only twin boundaries and dislocations in the system. At temperatures approaching \( T_m^\text{Cu} \), the sample represents a block of nearly dislocation-free single-crystalline copper.

Fig. 2 illustrates the drastic coarsening of the structure during an isothermal anneal at 750 K. The final structure obtained after 10 ns contains only a few twin boundaries and dislocations. As expected, the rapid grain growth is reflected in the temperature dependence of the order parameter \( \xi \) (Fig. 3). The latter rapidly increases during the first 1–2 ns of the anneal and reaches nearly 100% after several nanoseconds.
3.2. Alloy with uniform distribution of Ta

Structural stability of the Cu–6.5 at.% Ta alloy with uniform Ta distribution can be illustrated by comparing isothermal anneals at 750 and 1000 K. Fig. 4a shows the Ta distribution after the 750 K anneal for 24 ns. The distribution is totally random and reveals no correlation with GBs or other defects. Furthermore, it is virtually indistinguishable from the initial Ta distribution prior to the anneal. This result is not surprising, considering the practically "frozen" Ta diffusion in Cu at this relatively low temperature. Indeed, given the larger atomic size and much higher melting point of Ta, its diffusion in Cu is expected to be extremely slow in comparison with Cu self-diffusion.

The 750 K anneal did not produce any visible changes in the grain structure, as illustrated in Fig. 4b. This shows that the Cu–Ta alloy has a greater thermal stability than pure copper, which turns single crystalline after a much shorter anneal at this temperature. The order parameter $\xi$ increases during the early stages of the 750 K anneal. This increase indicates that, despite the stability of the grain structure, some relaxation processes continue to occur during the anneal. Such processes could be associated with changes in GB structure or rearrangement of dislocations reducing the system energy. These processes are usually controlled by self-diffusion of the majority element. That Cu self-diffusion is capable of creating non-negligible mass fluxes even at this relatively low temperature $0.567 T_m^{Cu}$ can be explained by short-circuit diffusion along GBs and dislocations.

By contrast, the 1000 K anneal causes extensive grain growth. The final structure obtained after 30 ns contains only twin boundaries and dislocations (Fig. 4c). The extensive grain growth correlates with the rapid increase in the order parameter during the first 10 ns of the anneal (Fig. 3). Once the GBs are gone, further increase in $\xi$ becomes extremely slow. This slow growth of $\xi$ reflects the sluggish migration kinetics of the twin boundaries and dislocations which are pinned by Ta atoms. It is interesting to note, however, that, despite the extensive structural changes and interactions of Ta atoms with moving GBs and dislocations, the distribution of Ta atoms in the structure remains fairly random. This observation indicates that the timescale of the present MD simulation was too short for the formation of Ta segregation at this temperature. This is confirmed by the simulations of Ta diffusion discussed in Section 5.

Comparing the isothermal anneals at 750 and 1000 K with the results for pure copper, it is obvious that the random distribution of Ta atoms in copper causes a significant retardation of grain growth at relatively low temperatures. However, it does not prevent grain growth at 1000 K and higher.

3.3. Alloy with Ta segregation

During the heating of the alloy with Ta segregation from 100 K to $T_m^{Cu}$, the grain structure “survived” until the alloy melted at a temperature close to $T_m^{Cu}$. This preliminary test
indicates that this alloy possesses an extremely high thermal stability in comparison with both pure Cu and the uniform Cu–Ta alloy. For a more detailed study, isothermal anneals were performed at the temperatures of 750 K (10 ns), 1000 K (70 ns), 1100 K (60 ns) and 1200 K (45 ns). Such long simulations were needed to better evaluate the alloy stability and to reveal the diffusion-controlled structural changes discussed below. Some of the results of the isothermal anneals are illustrated in Fig. 5 in images showing the Ta distribution in the final structures (images colored by centrosymmetry and CNA were also produced but are not shown here).

The isothermal anneal at 750 K did not produce any visible grain coarsening or redistribution of Ta atoms (Fig. 5a). In the final state, the Ta atoms continue to be distributed randomly within GB regions and triple lines, as they were in the initial state. As already mentioned, the fact that the Ta distribution remains unchanged is consistent with the extremely slow Ta diffusion at this temperature (Section 5).

The anneals at 1000 and 1100 K did not cause any substantial grain growth either. However, these anneals revealed important changes in the character of the Ta distribution, which are illustrated in Fig. 5b and c. It is observed that during the anneals the Ta atoms diffused along GBs and formed small clusters, of approximately 10–30 atoms, at GBs. At these temperatures, Ta atoms become sufficiently mobile to diffuse along GBs over distances on the order of a nanometer and agglomerate into clusters. The clustering occurs predominantly within the first several nanoseconds of the simulation and slows down thereafter.

Although the clustering process is already manifested in the images shown in Fig. 5, RDFs of Ta–Ta pairs were calculated to provide a more objective proof of the effect. To provide a baseline, Fig. 6a shows RDFs computed before and after the 750 K anneal in which the clustering was not detected. The prominent peak at 0.28 nm represents nearest-neighbor pairs, with lower peaks at larger distances coming from other coordination shells. It is clear that the RDF does not change during the 750 K anneal within statistical errors, confirming that the distribution of Ta atoms indeed remains unchanged. Furthermore, the relative positions of the peaks before and after the anneal are similar to those for Cu–Cu pairs (not shown here), suggesting that most of the Ta atoms are embedded in the fcc-type environment. By contrast, the 1100 K anneal produces a very large increase in the height of the first peak (Fig. 6b), which is strong evidence of clustering. In addition, the fcc peak at 0.5 nm splits into three sub-peaks corresponding to coordination shells of the bcc lattice. This splitting indicates that the atomic arrangement within the Ta clusters is similar to that in the bcc structure. Similar RDF changes were found after the 1000 and 1200 K anneals.

In addition to the changes in the spatial character of Ta segregation, some of the small grains underwent melting and subsequent crystallization at the beginning of the 1100 K anneal. As a result, they became part of a larger Cu grain and created a set of Ta clusters embedded in the copper lattice. Once the crystallization was complete, the structure did not change substantially for tens of nanoseconds.

Similar, but more extensive, melting and subsequent crystallization occurred during the 1200 K anneal. In this case, a liquid pocket “survived” for nearly 30 ns. During this time, the liquid developed a nanoemulsion structure similar to that found in [33]. Upon crystallization, the nanoemulsion created a disperse array of Ta clusters embedded in the Cu matrix. By the end of the anneal, the GBs completely disappeared and the final structure contained several twin boundaries and dislocations (Fig. 6c).
alloys at 1000 K. When Ta is segregated, $n$ shows only a moderate initial increase and soon reaches a stagnation at $\xi \approx 75\%$, which persists for over 50 ns. A similar trend was observed during the 1100 K anneal. Thus, Ta segregation greatly increases the grain stability in the Cu–Ta alloy in comparison with the uniform distribution of Ta. The grain structure remains stable up to at least 1100 K, whereas the uniform alloy suffers an extensive grain growth between 750 and 1000 K.

4. Tensile test results

The purpose of the tensile tests was to demonstrate the effect of Ta on the mechanical strength of the Cu–Ta alloys. Typical plots of the tensile stress $\sigma_{zz}$ vs. strain $\varepsilon_{zz}$ are shown in Fig. 7a for the particular case when the alloys were tested after a 10 ns anneal at 750 K. (It should be noted that the pure Cu was tested after partial relaxation at 300 K. The 750 K anneal eliminates the nanocrystalline structure due to rapid grain growth.) Two measures of strength were used. The first is the stress, $\sigma_Y$, at which noticeable deviations from linear-elastic deformation can be identified. This stress can be considered as a crude analog of the yield stress. The second measure of strength is the steady-state flow stress, $\sigma_f$, at which the curve reaches a plateau.

As expected, pure Cu is the softest of the three materials tested, with $\sigma_Y \approx 0.3$ GPa and $\sigma_f \approx 1.2$ GPa. Furthermore, examination of the structural snapshots saved during the test reveals that the tensile deformation causes significant coarsening of the grain structure at 300 K. Stress-induced grain growth in nanocrystalline materials was found in recent experiments [34–37], including nanocrystalline Cu [38,39]. The grain coarsening explains the sudden changes in the slope of the stress–strain curve, which are caused by disappearance of a grain or group of grains from the sample. By the time the strain reaches $\varepsilon_{zz} = 0.075$, the material becomes single crystalline, with a few remaining dislocations. Further deformation eventually produces multiple dislocations, an increase in $\sigma_f$ due to strain hardening, and other processes that are not relevant to the problem under study. The corresponding part of the stress–strain curve is not shown in Fig. 7a. The grain growth is also reflected in the behavior of the order parameter $\xi$, which increases during the deformation and reaches nearly 100% at $\varepsilon_{zz} = 0.075$ (Fig. 7b).
The alloy with uniform Ta distribution exhibits a higher strength with $\sigma_Y \approx 1.2$ GPa and $\sigma_f \approx 1.8$ GPa (Fig. 7a). The alloy with Ta segregation is even stronger, with $\sigma_Y \approx 1.5$ GPa and $\sigma_f \approx 2.3$ GPa. In both cases, the structure remains very stable and shows no grain coarsening during the deformation process. The order parameter $\xi$ decreases due to accumulation of dislocations, stacking faults and other defects inside the grains and near GBs. The tests performed on alloys after isothermal anneals at 1000 and 1100 K lead to similar conclusions. They confirm that Ta increases the strength of Cu, especially when the Ta atoms are segregated at GBs.

5. Grain boundary diffusion

In the GB diffusion simulations, we observed very linear plots of the mean-squared displacement vs. time. An example of such plots is shown in Fig. 8 for the temperature of 1200 K. The linearity of such plots confirms that the atomic displacements which we detect are indeed governed by diffusion kinetics. It should be noted, however, that the diffusion coefficients extracted from such plots vary from one time interval $\Delta t$ to another (Section 2), resulting in statistical error bars of the reported diffusivities.

The obtained GB diffusion coefficients are summarized in the Arrhenius diagram in Fig. 9. For Cu diffusion, our results are compared with recent simulations using the same GB and the same interatomic potential [29]. Excellent agreement is observed at all three temperatures, which validates our simulation methodology. Note that the statistical error bars of the present and previous [29] diffusivities are comparable to the size of the data points and are hardly resolved on the plot. Furthermore, encouraging agreement is observed with experimental data for GB self-diffusion in high-purity polycrystalline Cu [40], lending additional confidence to our calculations. These results also show that the presence of 10% Ta in the GB has little effect on Cu self-diffusion.

Note that the Ta diffusion coefficients have larger error bars in comparison with Cu. The poorer statistics of Ta
diffusion reflects the presence of only a small number of Ta atoms in the GB core. Despite the statistical errors, Fig. 9 clearly demonstrates that Ta GB diffusion in Cu is much slower than Cu self-diffusion. At the temperature of 1000 K, the difference between the respective diffusion coefficients exceeds two orders of magnitude. Although we chose not to compute the activation energy of Ta GB diffusion from only three data points, the plot strongly suggests that Ta has a higher activation energy than Cu. As a consequence, at temperatures below 1000 K, Ta diffusion is virtually frozen out.

Despite being significantly slower than Cu diffusion, the Ta diffusivity at the temperatures of 1100 and 1200 K becomes sufficient to cause the formation of the GB nanoclusters discussed in Section 3.3. For example, using the obtained GB diffusion coefficients, we estimate that at 1100 K the diffusion length of Ta atoms during a 50 ns anneal is approximately \(2\sqrt{Dt} \approx 1\) nm. This estimate is in good agreement with the observed size of the Ta clusters.

For bulk diffusion inside the grains, the root-mean-squared displacements of atoms were significantly below the first-neighbor interatomic distance \(r\). Furthermore, they did not scale linearly with time and were dominated by atomic vibrations. We conclude that the lattice diffusion of both Cu and Ta is negligible on the timescale of the present simulations. The upper bound of the diffusion coefficients estimated from the relation \(r^2/4t\) is on the order of \(10^{-12} \text{ m}^2/\text{s}\). The actual diffusivity of Ta is likely to be much smaller than this number. The negligible bulk diffusion explains why the samples with the initially uniform Ta distribution did not develop any detectable GB segregation during the thermal anneals (Section 3.2).

6. Grain boundary segregation

The equilibrium atomic structure of the \(\Sigma 5\) GB consists of identical kite-shaped structural units, as shown in Fig. 10. The zero-Kelvin segregation energies \(E_s\) at the substitutional sites labeled 1, 2, 3 and 4 were found to be \(-0.59\), \(-0.32\), \(-0.77\) and \(-0.20\) eV, respectively. For Ta atoms located further away from the GB, \(E_s\) rapidly approaches zero. Site 2 shows a positive segregation energy, meaning a strong repulsion of Ta atoms from this site. Site 3 is the site of the strongest segregation (negative \(E_s\) of the largest magnitude), followed by the next-strongest segregation at site 1. Segregation at interstitial sites was found to be highly unfavorable, with \(E_s = 1.33\) eV at site \(I\).

The degree of GB segregation can be quantified by the exponential factor \(s = \exp(-E_s/kT)\), where \(k\) is Boltzmann’s constant. For the highest temperature of our simulations (1200 K) we obtain \(s = 1714\) at site 3 and \(s = 300\) at site 1. This factor rapidly increases with decreasing temperature. These numbers refer to particular sites in one particular GB and were obtained by neglecting the possible temperature dependence of \(E_s\). Nevertheless, they demonstrate that even near the melting point of Cu, the Ta segregation tendency is extremely strong. For example, in alloys containing 0.1 at.\% Ta in the bulk, some of the GB sites are fully saturated with Ta even at 1200 K. At the temperature of 700 K, full GB saturation can be achieved already at the 50 ppm level of bulk Ta. This strong segregation tendency justifies our segregation model in which the Ta atoms were introduced into the GBs only.

7. Discussion

The MD simulations reported here were performed on nanocrystalline samples representing experimental as-milled structures and containing either pure copper or a Cu–6.5 at.% Ta alloy. Two types of Ta distribution in the alloy were tested: a purely random distribution; and segregation at GBs, dislocations and other defects. In the second case, most of the Ta atoms were residing at GBs
due to their large area. Structural stability of these materials was evaluated by a set of anneals at different temperatures.

On the timescale of the MD simulations, grain growth in pure Cu starts at temperatures of about 0.47$T_m$. This corresponds to even lower temperatures on the experimental timescale. Experiments indicate the onset of grain growth in polycrystalline Cu at temperatures between 420 and 550 K ($0.32 - 0.42T_m$) [41-48]. The introduction of Ta atoms causes a strong retardation of the grain growth. Even for a uniform distribution of Ta, the grains begin to grow at temperatures of about (0.6–0.7)$T_m$. In the alloy with GB segregation, the Ta effect is truly remarkable: the pinning of GBs becomes so strong that the usual grain growth by capillary-driven GB migration is not observed at any temperature up to $T_m$. Instead, as the temperature approaches $T_m$, the smallest grains melt and recrystallize in a new crystallographic orientation continuing the orientation of a neighboring larger grain. It is this unconventional mechanism that eventually leads to the coarsening of the structure and the overall encapsulation of the Ta clusters inside the grains at temperatures above (0.85–0.9)$T_m$. We expect that this mechanism would cease to operate as the grain size increases, but this prediction is yet to be tested.

The resistance to grain growth observed in the samples with uniform Ta distribution can be explained by additional dissipation due to the interaction of moving GBs with Ta atoms. At high temperatures and on experimental timescales, this interaction could lead to the formation of GB segregation and thus the retardation of GB motion by the solute drag effect [49-51]. On the timescale of the present MD simulations, the extremely slow Ta diffusion prevented the formation of any noticeable GB segregation. In terms of the solute drag models by Cahn [49] and Lücke and Stüwe [50], the GB motion implemented in our simulations was in the break-away regime corresponding to relatively weak friction forces. Due to this timescale limitation, our simulations are likely to underestimate the effect of the random Ta distribution on grain stability. On the other hand, when Ta segregation was created in the starting configuration, the GBs became completely pinned and did not practically move during the simulations. Again, we cannot exclude that GB migration could still occur on much longer timescales, in which case their kinetics could be described by the classical solute drag models [49,50] or their extensions, including saturation and solute-solute interactions [51].

An important finding of the simulations is the formation of Ta nanoclusters at GBs during high-temperature anneals. The clusters form by short-circuit diffusion of the segregated Ta atoms along GBs. They are somewhat reminiscent of the nanoeulsion found in recent MD simulations of liquid Cu–Ta alloys using the same interatomic potential [33]. The clusters appear to have a relatively narrow distribution of sizes and their coarsening was not observed on the timescale of the present MD simulations. The Ta clusters strongly pin GBs, preventing their migration. Once the clusters are formed, the structural evolution reaches a complete stagnation, as illustrated by the 1000 K curve in Fig. 3. Stabilization of Cu GBs by Ta particles, although with larger sizes, has been observed experimentally in Cu–Ta alloys (see e.g. [4] and Fig. 1) and other immiscible copper-refractory systems [2,5]. The mechanism of this stabilization can be explained in terms of the Zener pinning effect. In our simulations, the pinning pressure apparently dominated over the capillary driving force and depinning events were never observed.

Simulated tensile tests were performed to demonstrate the profound impact of Ta alloying on mechanical strength. As expected, it was found that the addition of Ta strongly increases the yield and flow stresses, especially when Ta is segregated at GBs or forms nanoclusters. Much of the strengthening effect is simply due to the preservation of the small grain size and can be explained by the usual deformation mechanisms in polycrystalline metals [52]. However, an additional strength may come from the restraining effect imposed by the segregated Ta atoms and their clusters on GB sliding, slip transfer and other GB processes.

Although detailed mechanisms of Ta segregation and nanoparticle formation are not fully established, the following plausible scenario emerges from our simulations and recent experiments. During the ball milling, a certain percentage of Ta atoms is forced into the copper lattice, with the remaining Ta forming separate grains. During the subsequent heat treatment, partial growth of copper grains occurs, along with dislocation rearrangements and other recovery processes. As the moving GBs and dislocations sweep through the lattice, Ta atmospheres form and eventually lead to GB segregation. An additional amount of Ta can be supplied to GBs by diffusion along dislocation lines (dislocation-enhanced diffusion [31]). As the material is annealed further, the supersaturated Ta segregation begins to form nanoclusters, a process which requires diffusion-controlled redistribution of Ta inside GBs. We emphasize that this process is only possible due to the phenomenon of fast diffusion along GBs [31]; it could not occur in the Cu lattice, where Ta diffusion is extremely slow even near $T_m$. As mentioned earlier, the tendency to form nanoclusters may have the same atomic origin as the formation of stable nanoelemulsions found in liquid Cu–Ta alloys [33]. This possible connection is supported by the highly disordered structure of many GBs at high temperatures. Such disordered boundaries offer a "liquid-like" environment for nanocluster formation and provide high-diffusivity pathways for Ta redistribution [28]. Since experiments show the formation of Ta particles with sizes of a few nanometers and larger, we assume that the nanoclusters eventually transform to larger particles, which then continue to grow by the Ostwald ripening mechanism.

Further experiments and simulations are essential for testing this scenario. On the simulation side, implementing
larger systems and longer MD times may help verify the formation of Ta segregation at moving GBs and reveal the evolution of the nanoclusters into nanoparticles. Additional insights can be obtained by further simulations of equilibrium Ta segregation at Cu GBs and thermodynamic calculations of the segregation effect on the GB free energy. The timescale problem inherent in MD simulations of diffusion can be readily overcome by applying the semi-grand-canonical Monte Carlo method, which quickly brings the system to thermodynamic equilibrium by swapping atomic species [53–55].

Acknowledgements

This work was supported in part by the US Army Research Laboratory under Contract W911QX-11-P-0187. Additionally, the authors would like to recognize Mr. Brady G. Butler for performing the TEM examination of the ball-milled Cu–10 at.% Ta sample.

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