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Atomistic modeling of capillary-driven grain boundary motion in Cu-Ta alloys

R.K. Koju^a, K.A. Darling^b, K.N. Solanki^c, Y. Mishin^{a, *}

^a Department of Physics and Astronomy, George Mason University, MSN 3F3, Fairfax, VA 22030, USA

^b Army Research Laboratory, Weapons and Materials Research Directorate, APG, MD 21014, USA

^c School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85287, USA

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ABSTRACT

Nanocrystalline Cu-Ta alloys are emerging as a new class of structural materials preserving the nanoscale grain size up to the melting point of Cu. This extraordinary structural stability is caused by the strong pinning of grain boundaries (GBs) by Ta nano-clusters precipitating from the unstable solid solution after mechanical alloying. Many aspects of the Ta stabilization effect remain elusive and call for further experimental and simulation work. In previous atomistic computer simulations of stress-driven GB migration [JOM **68**, 1596 (2016)], the GB–cluster interactions in Cu-Ta alloys have been studied for several different compositions and GB velocities. The results have pointed to the Zener pinning as the main mechanism responsible for the grain stabilization. This paper extends the previous work to the motion of individual GBs driven by capillary forces whose magnitude is similar to that in real nanocrystalline materials. Both the impingement of a moving GB on a set of Ta clusters and the GB unpinning from the clusters are studied as a function of temperature and alloy composition. The results demonstrate a quantitative agreement with the Zener pinning model and confirm the "unzip" mechanism of unpinning found in the previous work. In the random Cu-Ta solid solution, short-circuit Ta diffusion along stationary and moving GBs leads to the nucleation and growth of new GB clusters, which eventually stop the GB motion.

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1. Introduction

Many beneficial properties of nanocrystalline materials owe their origin to the large specific area (per unit volume) of grain boundaries (GBs) and other internal interfaces. One of such properties is the high mechanical strength. The strengthening effect is partially caused by the formation of dislocation pileups stopped at GBs [1]. However, at small enough grain sizes the dislocation sources inside the grains cease to operate and the dislocation pileups cannot form. Instead, the plastic deformation is predominantly controlled by GB processes such as GB sliding and grain rotation [2–11].

Wider applications of nanocrystalline alloys are hampered by the onset of grain growth at elevated temperatures. In some of the nanocrystalline materials, substantial grain growth can even occur at room temperature. The driving force for the grain growth has a

* Corresponding author. E-mail address: ymishin@gmu.edu (Y. Mishin).

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capillary nature and depends on the excess free energy of GBs. Since the specific GB area in nanocrystalline materials is large, the capillary driving force is strong and increases as the grains become smaller. The grain growth results in deterioration of the superior properties of nano-materials.

Several approaches have been proposed for reducing the grain growth, the most effective of them being alloying. There are two possible mechanisms by which alloying can stabilize nano-grains. The thermodynamic stabilization can be achieved by reducing the GB free energy γ by solute segregation [12–23]. Since the capillary driving force is proportional to γ , the grain size can be preserved for a longer time and/or up to higher temperatures. It has even been suggested that the total free energy may reach a minimum at a finite grain size, producing a thermodynamically stable nano-grained material [13,14,16,18,20–22,24–26]. The kinetic stabilization is achieved by the reduction in the GB mobility by the solute drag effect [23,27–29] or by the Zener pinning of GBs by small precipitates of a second phase [23,29–35]. Clean separation of the thermodynamic and kinetic factors is very difficult. In many cases, the grain stabilization is likely to be a combined effect of both







mechanisms.

Nanocrystalline Cu-Ta alloys have recently attracted much attention due to their extraordinary structural stability and strength at high temperatures [35–42]. FCC Cu and BCC Ta are practically immiscible in the solid state. High-energy mechanical alloying produces an unstable solid solution of the two elements, which decomposes during the subsequent thermal processing. Ta atoms precipitate from the solution in the form of nanometer-scale clusters coherent with the Cu matrix. These clusters strongly pin GBs by the Zener mechanism, preventing further grain growth. As a result, a Cu-Ta alloy can preserve the grain size of about 100 nm at high temperatures up to the melting point of Cu. The discovery of this fully stabilized nano-structure opens an avenue for the design of a new class of materials for high-temperature, high-strength applications.

The grain size stabilization leads to unique mechanical properties of Cu-Ta alloys, such as the high strength (above 1 GPa) and small strain-rate sensitivity under tension and compression [38], the lack of superplastic behavior, and excellent creep resistance [43]. The Ta clusters located inside the grains can contribute to the strengthening by restraining the dislocations glide and twinning. The clusters residing at GBs can block the dislocation transmission and enhance the Hall–Petch mechanism of hardening [1]. In addition, the GB clusters create obstacles to the operation of GB deformation mechanisms by suppressing GB sliding and grain rotation.

Cu-Ta allovs also present an ideal model system for understanding the general principles of grain stabilization. The Ta atoms do not follow the classical segregation model wherein the solute atoms form a relatively uniform distribution over the GB area and reduce the GB free energy. Instead, the Ta atoms form a chain of discrete nano-clusters attached to the GBs and separated by areas of pure Cu boundaries, as illustrated in Fig. 1 for the Cu-3at.%Ta alloy. The upper left corner of the image in Fig. (a) shows a grain decorated with Ta clusters, with a more detailed view of the clusters shown in Fig. 1(b). Since the clusters only occupy a small fraction of the total GB area,¹ they are unlikely to reduce the GB free energy substantially as assumed in the thermodynamic stabilization models. On the other hand, they can be very effective in blocking the GB motion by the Zener pinning mechanism [30–34]. This presents us with an opportunity to gain a better mechanistic understanding and evaluate the strength of the kinetic stabilization mechanism separately from the thermodynamic factor.

The previous atomistic simulations [35] have confirmed that Ta clusters in Cu-Ta alloys can exert a strong pinning force and can totally arrest the GB motion. The stress behavior during the GB–cluster interactions was found to be well-consistent with the Zener model [30–34]. The GB migration was driven by an applied shear stress causing the GB motion by the shear-coupling mechanism [44,45]. It was noted that the applied stresses driving the GB motion were rather large and the speeds of GB migration were orders of magnitude higher than the typical speeds under experimental conditions.

The main goal of the present work was to demonstrate that the conclusions reached in the previous study [35] are independent of the particular driving forces or GB migration rates implemented there. To this end, we perform systematic atomistic simulations of GB motion driven solely by the capillary pressure. The grain sizes studied here are typical of many nanocrystalline materials. Accordingly, the capillary driving force applied to the GBs is



(b) **Fig. 1.** High resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of a Cu-3at.%Ta alloy consolidated by equal channel angular extrusion (ECAE) at 700°C. The Ta clusters are revealed by Z-contrast. The average Cu grain size is about 86 nm. (a) A typical grain decorated with Ta clusters; (b) Zoom-in new showing Ta clusters residing at and near GBs. The approximate GB positions are outlined by dashed lines.

representative of typical forces existing in real materials. In addition to the modeling of GB-cluster interactions, we investigate the role of GBs in the precipitation of Ta clusters during the decomposition of the unstable Cu-Ta solution. This precipitation process is accompanied by a dynamic instability of the GB motion and eventually leads to GB arrest when the growing clusters reach a critical size.

2. Methodology

Atomic interactions were described by the recently constructed angular-dependent interatomic potential for the Cu-Ta system [46]. A rectangular simulation block was initially filled with perfect FCC Cu lattice and had the dimensions $31.8 \times 31.8 \times 7.3$ nm (599,760 atoms) with periodic boundary conditions. A cylindrical grain with a radius 9.99 nm was created at the center of the block by rotating its lattice around the [001] direction *z* by an angle θ_0 (Fig. 2). The atomic structure of the tilt GB obtained was equilibrated by minimizing its energy with respect to removal, addition and

¹ The images in Fig. 1 show the projections of Ta clusters in the TEM foil on the plane parallel to the page. The actual, three-dimensional number density of the clusters is much smaller than it appears on the images.



Fig. 2. Simulation block containing a cylindrical grain. The Cu atoms are shown in the cyan color. The GB (blue) is decorated with a set of Ta clusters (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

displacements of atoms as described elsewhere [5].

In addition to the pure Cu system, Cu-Ta alloys were created with three different types of Ta atom distributions. In the first case, Ta was introduced into the GB region by composition-controlled semi-grand canonical Monte Carlo (MC) simulations using the parallel MC code ParaGrandMC [47]. The temperature of the MC simulations was chosen to be 900 K. The trial moves of the MC algorithm included small random displacements of randomly selected atoms in a random direction with simultaneous random reassignment of chemical species to either Ta or Cu. In addition, the system dimensions were randomly rescaled. This rescaling ensured zero-stress conditions during the simulations, which helped to minimize the effect of the large atomic size difference between Cu and Ta. The trial moves were accepted or rejected by the Metropolis criterion [48]. Due to the negligible mutual solid solubility in the Cu-Ta system, Ta nano-clusters only formed in the GB region. In the composition-controlled mode of the MC algorithm [46,47,49], there is a feedback loop between the composition and the chemical potential difference between the species that ensures equilibration to a given chemical composition of the system. This allowed us to create a set of alloys with several targeted chemical compositions. In the following, these compositions will be measured by the atomic percentage of Ta atoms averaged over the entire simulation block. Given that the Ta atoms are actually located in the GB region, such compositions do not represent the GB chemistry and only serve to label its different chemical states.

In the second case, the chemical species were only switched during the MC simulations within a 3 nm thick concentric cylindrical shell with a radius smaller than the radius of the grain. The Ta-rich shell obtained mimicked the Ta distribution left behind by an imaginary smaller grain that had been able to detach from this distribution and disappeared. This configuration was created to study the GB interaction with Ta clusters as the grain shrinks by capillary forces. As in the previous case, several alloy compositions were created.

Finally, in the third case several non-equilibrium solid solutions were created by randomly substituting Cu atoms by Ta atoms uniformly across the entire simulation block until a prescribed chemical composition was reached. Such random solutions represented the state of the material after the mechanical alloying and prior to the thermal treatment.

Starting with the initial configuration, the system evolution was studied by molecular dynamics (MD) simulations. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [50] was utilized. The isothermo-isobaric (NPT) ensemble was implemented at several temperatures between 750 and 1100 K under zero pressure conditions. The latter condition ensured that no internal stresses arose in the simulation block due to the volume change caused by reduction in the GB area. Snapshots of the simulation block were saved at regular time intervals recording the coordinates, velocities, energy and stress components of individual atom. The GB position was tracked using the bond angle analysis implemented in the OVITO visualization software [51]. The effective radius of the grain was calculated by averaging the distance to the GB atoms from their centroid. Changes in the lattice orientation of the grain were tracked using four nearest neighbors lying in the (x, y) plane for lattice atoms inside and outside the grain (0.8 nm away from the GB). The minimum rotation angle between the sets of the four vectors pointing to the neighbors was averaged over the inner atoms of the grain and taken as the misorientation angle θ across the GB.

3. Results

3.1. Grain shrinkage and rotation in pure Cu

To provide a baseline for comparison with Cu-Ta alloys, simulations were first conducted on the pure Cu system. As expected, the grain was found to shrink and eventually disappear. Simultaneously, the lattice of the inner grain was found to rotate towards larger misorientation angles. Fig. 3 shows the results for the initial misorientation angle $\theta_0 = 28.07^\circ$. In this figure and all similar plots, the data points were collected from individual snapshots. The GB area decreases as a linear function of time following the parabolic kinetics predicted by theoretical models [5,44]. Slight deviations from the parabolic kinetics are observed when the grain becomes small (Fig. 3(a)). This acceleration of the shrinkage process could be due to an increase in the curvature-dependent GB free energy. The rate of GB shrinkage increases with temperature.

The grain rotation in Fig. 3(b) is expected from the shearcoupling theory [44,45,52,53]. The theory predicts that coupled motion of a curved GB creates a driving force for relative rotation of the two grains. For tilt GBs, this rotation should occur towards larger misorientation angles. This predicted mode of rotation was indeed observed in previous MD simulations [5,54] and is confirmed in this work. At all temperatures studied here, the GB remained shear-coupled and rotated towards the angle of about 36°. This special angle is associated with the discontinuity in the misorientation dependence of the coupling factor [5,45,52,53,55]. These results are in full agreement with previous work, which lends additional confidence to the simulation methodology used in this paper.

3.2. GB pinning by Ta clusters

When Ta was introduced into the GB region and the latter was equilibrated by MC simulations, Ta was found to form a distribution of discrete clusters with an approximate size of about a nanometer (20–25 atoms) decorating the GB (Fig. 2). Increase in the alloy composition only produced more clusters with little effect on their average size or size distribution. The tendency of Ta atoms to preserve the cluster size was also observed in previous simulations



Fig. 3. The grain area (a) and the misorientation angle θ (b) as functions of time during MD simulations of pure Cu at several temperatures. The initial misorientation angle is $\theta_0 = 28.07^{\circ}$.

[35–37,39–42] and experiments [35,37,38,40–42]. In the present work, the cluster size was measured by the effective radius $r = (3n\Omega/4\pi)^{1/3}$, where Ω is the atomic volume of the alloy and *n* is the number of atoms in the cluster. The average cluster radius is reported in Table 1 as a function of alloy composition at 900 K. As Ta concentration increases, *r* only changes from 0.39 nm to 0.44 nm, whereas the number *N* of Ta clusters increases in proportion to the concentration and reaches N = 33 at the highest concentration studied here (0.15 at.%Ta).

When the number of clusters is small, the capillary force easily unpins the GB from the clusters. The grain then shrinks and rotates toward the 36° misorientation, as it does in pure Cu (Fig. 4). The initially small slopes of the curves in Fig. 4 reflect the unpinning process. Once the GB is unpinned, its further evolution follows the same parabolic kinetics as in pure Cu.

Table 1	
Characteristics of GB clusters as a function of alloy composition at 900 K.	

Alloy composition (at.%Ta)	Ν	<i>r</i> (nm)	GB area per cluster (nm ²)
0.05	15	0.39	30.76
0.06	16	0.41	28.84
0.07	19	0.41	24.28
0.08	24	0.39	19.22
0.09	25	0.40	18.46
0.10	28	0.40	16.47
0.15	33	0.44	13.98



Fig. 4. The grain area (a) and the misorientation angle θ (b) as functions of time in MD simulations of the grain pinned by Ta clusters at 900 K. The alloy compositions (at.%Ta) are indicated in the legend.

The unpinning does not occur uniformly along the GB but rather follows the "unzipping" mechanism illustrated in Fig. 5. The GB initially unpins from one random cluster and the free GB segment obtained tries to migrate toward the grain center, exerting additional pulling forces on the neighboring clusters. These neighbors eventually also let the GB go and the free segment becomes longer. This unzipping process propagates along the GB, unpinning one cluster at a time, until the entire GB detaches from the set of clusters and continues to shrink and rotate in the pure Cu environment. While the grain area decreases during the unpinning process, the grain rotation remains blocked until the GB completely separates from the clusters. This explains the nearly horizontal portions of the curves in Fig. 4(b).

As the Ta concentration increases, the pinning effect of the clusters becomes stronger. The GB takes an increasingly longer time to unpin and the grain rotation period becomes shorter (Fig. 4). In the 0.15 at.%Ta alloy containing the total of 33 GB clusters, the GB is unable to unpin on the timescale of the present simulations.

It is interesting to compare the simulation results with predictions of the Zener model of GB pinning [30–34]. According to this model, the GB motion is blocked when the driving pressure due to the GB curvature is balanced by the pinning pressure exerted on the GB by the disperse particles. The maximum pinning force created by a single spherical particle is $F_{max} = \pi r \gamma$, where *r* is the particle radius. For *N* particles interacting with a GB of area *A*, the maximum pinning pressure is $P_p = \pi r \gamma N/A$. In our case $A = 2\pi RL$, where *R* is the radius of the cylindrical grain and *L* is its thickness in



Fig. 5. The unpinning mechanism in the Cu-0.05%Ta alloy at 900 K. (a) Ta clusters (yellow) are initially located at the GB (blue). (b) The GB has unpinned from 2 clusters and the unpinning process propagates along the GB. (c) The GB has unpinned from most of the clusters. (d) The GB has totally unpinned from the clusters. FCC Cu atoms are not shown for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the *z* direction. For the capillary pressure $P_c = \gamma/R$, the pinning condition $P_p = P_c$ gives

$$N = \frac{2L}{r}.$$
 (1)

Inserting L = 7.3 nm and r = 0.44 nm (Table 1), the grain should be pinned in its initial state by $N \approx 33$ clusters. This number exactly matches the number of clusters blocking the grain in the 0.15 at.%Ta alloy.

This perfect agreement may seem surprising since the Zener model is based on many assumptions and approximations [32]. For example, the equation for F_{max} that we utilized above assumes that the particle-matrix interface is incoherent. More generally, $F_{max} = \alpha r \gamma$ and Eq. (1) becomes $N = 2\pi L/\alpha r$, where α is a numerical factor. For incoherent particles $\alpha = \pi$, while for coherent $\alpha = 2\pi$ [56]. On the other hand, keeping the particles incoherent but taking into account the GB curvature, $\alpha \approx 3.96$ [57]. Given the approximate character of the model and the fact that the boundary was only pinned on the relatively short timescale of the MD simulations, the perfect agreement is likely to be fortuitous. Nevertheless, this agreement does indicate that the GB pinning observed in the present simulations is generally consistent with the Zener mechanism.

Fig. 6 shows the results of similar simulations at four different temperatures (800 K, 900 K, 1000 K and 1100 K) at a fixed alloy composition (0.08 at.%Ta). As expected, the rates of GB migration and grain rotation increase with temperature. In addition, the unpinning time manifested by the horizontal portions of the curves becomes shorter at higher temperatures. These trends reflect the thermally activated nature of the unpinning process and of the coupled GB migration/rotation process.

In the preceding simulations, the Ta clusters were created at the GB from the very beginning. To demonstrate that our conclusions do not depend on the initial conditions, a similar distribution of clusters was created within a cylindrical shell inside the grain (Fig. 7). As mentioned above, one can think of such clusters as left behind by another GB that was pinned by them but was able to escape and migrated elsewhere. In this simulation setup, the GB was expected to start moving in the pure Cu region and eventually hit the cluster distribution. This was indeed observed in the simulations. The grain rotated from the initial $\theta_0 = 28.07^{\circ}$ misorientation to about 33° before encountering the clusters. When the alloy concentration, and thus the number of clusters, were small, the boundary was able to unpin from the clusters and continued to shrink until the grain collapsed into a point. The GB-cluster interaction only caused a temporary hold of the shrinkage process, manifested in the horizontal portions of the area-time and angletime curves (Fig. 8). The unpinning occurred by the previously discussed unzip mechanism.

At higher Ta concentrations, the GB took a longer time to unpin and was eventually stopped by the clusters when the alloy composition reached 0.21 at.%Ta. The previous calculations from equation (1) predicted that 33 clusters should be sufficient to block the GB migration. However, as indicated in Table 2, the actual number of GB clusters in the 0.21 at.%Ta alloy is 43. In addition to the approximate character of the Zener model mentioned above, the discrepancy could be caused by the significantly larger surface density of the clusters in the cylindrical shell than in the initial GB (cf. Table 1). Under the high-density conditions, the clusters can no longer be treated as isolated as assumed in the Zener model. The contact angles between the clusters and the short GB segments



Fig. 6. The grain area (a) and the misorientation angle θ (b) as functions of time in MD simulations of the grain pinned by Ta clusters in the 0.08 at.%Ta alloy at different temperatures (indicated in the legend).



Fig. 7. Typical initial configuration of Ta clusters forming a cylindrical shell inside the grain. The grain shrinks and rotates until the GB (blue) hits the clusters (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 8. The grain area (a) and the misorientation angle θ (b) as functions of time during MD simulations of the grain containing a set of Ta clusters at 900 K. The alloy compositions (at.%Ta) are indicated in the legend. The initial misorientation angle is $\theta_0 = 28.07^{\circ}$.

Table 2

Characteristics of Ta clusters in the cylindrical shell inside the grain as a function of alloy composition at 900 K.

Alloy composition (at.%Ta)	Ν	<i>r</i> (nm)	GB area per cluster (nm ²)
0.06	17	0.39	13.07
0.08	24	0.38	8.71
0.11	30	0.41	7.11
0.15	45	0.39	4.84
0.17	44	0.41	4.97
0.19	46	0.42	4.66
0.21	43	0.44	5.40
0.23	45	0.44	4.88

connecting them could no longer reach 45° corresponding to the maximum pulling force. This could reduce the increase in the pinning efficiency per each added cluster. Another potential source of discrepancy is the elastic strain field around the clusters [58], which is not in the Zener model. Considering these uncertainties, the simulation results can be considered compatible with the Zener model at least on a semi-quantitative level.

3.3. GB motion and grain rotation in random solid solution

Randomly distributed Ta atoms inserted in the Cu matrix imposed a drag force that reduced the rates of GB migration and



Fig. 9. The grain area (a) and the misorientation angle θ (b) as functions of time in MD simulations of a random Cu-Ta solution at 900 K. The alloy compositions (at.%Ta) are indicated in the legend.

grain rotation in comparison with pure Cu. This drag effect was not as strong as the pinning effect of the clusters. Much higher Ta concentrations were required to achieve the same level of retardation. The effects of the alloy composition and temperature are illustrated in Figs. 9 and 10, respectively. It is evident that the addition of Ta significantly reduces the rate of GB migration and strongly suppresses the grain rotation. The capillary driving force γ/R increases as the grain shrinks, which explains the accelerated shrinkage rate in the end of the simulation when the grain becomes small. At this final stage, the grain rotation is accelerated as well.

An interesting feature of GB migration in the random alloy is the stop-and-go character manifested in the stepwise shape of the area-time curves (Figs. 9 and 10). This stop-and-go behavior is especially pronounced at higher Ta concentrations and/or lower temperatures. A similar effect was observed in the recent simulations of stress driven GB motion in the random Cu-Ta solution [35]. The mechanism of this effect is related to the formation of small GB clusters by short-circuit diffusion of Ta atoms along the GB. Such clusters pin the GB and it stops for a period of time during which the cluster formation continues to occur. The boundary eventually breaks away from the clusters, makes a fast move forward, but soon slows down due to the drag force. This allows the short-circuit diffusion to start the formation of a new set of clusters. These clusters eventually stop the boundary and the whole process repeats. As a result, the GB evolution consists of alternating periods of rapid motion and arrest. The dynamic instability of this process makes it similar to the dynamic strain aging phenomenon [59], the



Fig. 10. The grain area (a) and the misorientation angle θ (b) as functions of time in MD simulations of random 1.25 at %Ta solution at different temperatures (indicated in the legend).

Portevin-Le Chatelier effect [60], and other cases of stick-slip behavior.

The process just described must create an array of Ta clusters behind the moving GB. This was indeed observed in the simulations as illustrated by two examples in Fig. 11. In the 1.25 at.%Ta solution at 900 K, the boundary shrinks in the stop-and-go regime and collapses into a point after 8.8 ns. Fig. 11(a) shows the clusters formed during this time. While two clusters precipitated outside the grain, most of them formed in the area swept by the GB motion. The chain of clusters in the upper right corner of this area was created by a GB segment that remained pinned at this location for a longer period of time than other segments. In the solution containing 1.5 at.%Ta at the same temperature, the GB quickly shrinks by about a nanometer, after which it stops and becomes permanently pinned by the clusters. For the rest of the simulation run (90 ns), the boundary only serves as a short-circuit path for cluster growth, causing the formation of many new clusters (Fig. 11(b)).

While the increase in the rate of cluster formation (and thus the stop-and-go GB motion) with Ta concentration is readily understood, the effect of temperature is less predictable. Higher temperatures increase the rate of GB diffusion needed for the cluster formation. On the other hand, at high temperatures the GB moves faster and unpins from the clusters more easily, leaving the GB less time to grow the clusters. The simulations indicate that the second trend dominates over the first: low temperatures favor the cluster formation due to the slow GB motion, even though the Ta diffusivity inside the GB is slower.



Fig. 11. Ta cluster precipitation from the Cu-Ta random solution in MD simulations at 900 K. The dashed circle shows the initial GB position. (a) 1.25 at.%Ta solution after the GB shrinks to a point. Only clusters containing more than 4 atoms are shown. (b) 1.5 at.%Ta solution where the GB stopped after a short period of migration. Only clusters containing more than 5 atoms are shown.

4. Discussion and conclusions

In the previous work [35], the GBs were driven by applied shear stresses coupled to the GB motion. By contrast, the present study was focused on the motion of curved GBs driven by capillary forces. The latter process is more relevant to the structural stability problem since the grain growth in polycrystalline materials is caused by capillary forces.

In conventional, coarse-grained polycrystalline materials, the capillary driving force (pressure) is on the order of 10^3 to 10^5 Pa [61]. In nanocrystalline materials, this force can be much larger. Assuming $\gamma \approx 1$ J/m² and taking the initial grain radius $R \approx 10$ nm studied here, the estimated capillary pressure is about $\gamma/R \approx 100$ MPa. Nanocrystalline materials with grain diameters of about 20 nm are not unusual, thus the pressures implemented in this work are quite realistic. In typical Cu-Ta alloys, the grain diameter is around 100 nm (see example in Fig. 1) and thus the capillary pressure $2\gamma/R$ is about 40 MPa. Under such conditions, the pinning effect of the Ta clusters is even more prominent than it was

observed in this paper. For example, the existence of just one Ta cluster per $3.5 \times 3.5 \text{ mm}^2$ of the GB area can be sufficient for blocking the grain growth at 900 K (Table 1).

The GB pinning effect observed in this work is consistent with the Zener model [23,29–35]. The simulations strongly suggest that the outstanding structural stability of the Cu-Ta alloys is solely due to the kinetic mechanism. Although the material is thermodynamically unstable, the extremely low GB mobility prevents the grain growth at any temperature up to the melting point.

A unique feature of the Cu-Ta alloys in comparison with many traditional dispersion-strengthened materials is that the Ta clusters show very little, if any, coarsening at high temperatures. As noted previously [35-37,39-42] and confirmed in this paper, the Ta cluster size is extremely stable. Adding more Ta to the alloy only results in the formation of more clusters with nearly the same size. The physical origin of this remarkable property of Ta atoms in Cu is not well understood. Simulations show that Ta and Cu form a thermodynamically stable nano-colloidal structure in the liquid state [62], with the Ta cluster size comparable to that in the solid state. This tendency to preserve the cluster size is thought to be related to a unique structure and energetics of Cu-Ta interfaces. It was suggested [62] that the Cu-Ta interactions across the interfaces favor a spontaneous interface curvature, which dictates the most stable particle size. It was also suggested that the resistance to coarsening or coalescence might be an indicator of a negative interface tension that nevertheless keeps the structure stable due to the strong curvature effect [62]. More research is needed to better understand this unusual effect on the atomic level and explore its existence in other immiscible systems.

The simulations have shown that the precipitation of Ta clusters from the unstable solid solution occurs by heterogeneous nucleation at GBs. For stationary boundaries, the process involves Ta diffusion to the boundary from nearby lattice regions followed by fast redistribution by short-circuit diffusion. As a result, the boundaries become permanently pinned in place by the clusters. Moving GBs cannot nucleate so easily. At early stages they only experience a solute drag force. The latter slows them down until small clusters begin to nucleate. This creates a snowball effect in which the clusters reduce the GB speed and permit the formation of more clusters. Some of the GBs become permanently pinned, while others break away from the clusters and continue to migrate, only to be slowed down and pinned again.

In addition to the formation of GB clusters, the process described above creates Ta clusters inside the grains. Such clusters may continue to grow until they reach the optimal size. Some of them eventually stop the motion of other moving boundaries (as observed in this paper) and become GB clusters, while others still remain inside the grains. The existence of Ta clusters inside the grains is well documented in recent experiments [37,38,40–42] (Fig. 1) and is one of the contributors to the high strength and unprecedented creep resistance [43] of the Cu-Ta alloys.

Some of the clusters located inside the grains can pin lattice dislocations. In fact, dislocations themselves could serve as cluster nucleation sites in addition to GBs, but this hypothesis requires validation by experiment and/or simulations in the future.

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