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# RPPR Final Report
as of 08-Sep-2018

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**Major Goals:** Nano-crystalline immiscible metallic alloys are very promising structural materials combining high mechanical strength with extraordinary structural stability at high temperatures. The goal of the proposed research is to develop a fundamental understanding of the physical mechanisms responsible the thermal stability and strength of immiscible alloys focusing on the Cu-Ta system as a specific model. To achieve this goal, new computer simulation approaches will be developed for prediction and optimization of thermal and mechanical properties of immiscible alloys. Using a wide range of advanced atomistic simulation methods, a systematic study of thermodynamic properties and kinetic characteristics of grain boundaries (GBs) in Cu-Ta alloys will be conducted. This will include calculations of key properties of GBs as the GB free energy, GB diffusivity, GB mobility and GB resistance to deformation and sliding. These simulations will be performed on both polycrystalline samples, representing collective behavior of multiple GBs, and on individual crystallographically characterized boundaries in order to establish a link between GB structure, GB crystallography, and thermodynamic and kinetic factors of thermal stability. This work will provide the fundamental knowledge needed for optimization of synthesis and processing routes of Cu-Ta alloys and for discovery of new high-strength immiscible alloy systems in the future. The proposed research is synergistic with experimental work on immiscible structural alloys currently underway at the Army Research Laboratory.

**Accomplishments:** See PDF file attached with a detailed description of accomplishments.

**Training Opportunities:** The postdoc and PhD student supported by this grant have been trained in a large spectrum of atomistic simulation methods, ranging from the construction of classical interatomic potentials to the implementation of large-scale MD and Monte Carlo simulations of structural evolution, diffusion and mechanical behavior of alloys. They further expanded their knowledge of the field by attending a number of workshops and conferences and giving presentations.

# RPPR Final Report
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**Results Dissemination:** The results obtained in this project have been presented in the journal publications:

Tanaporn Rojhirunsakool, Kristopher A. Darling, Mark A. Tschopp, Ganga P. Purja Pun, Yuri Mishin and Laszlo J. Kecskes: Structure and thermal decomposition of a nanocrystalline mechanically alloyed supersaturated Cu–Ta solid solution, MRS Communications 5, pp. 333-339 (2015).

G. P. Purja Pun, K. A. Darling, L. J. Kecskes and Y. Mishin: Angular-dependent interatomic potential for the Cu-Ta system and its application to structural stability of nano-crystalline alloys, Acta Materialia, 100, 377-391 (2015).

B. C. Hornbuckle, T. Rojhirunsakool, M. Rajagopalan, T. Alam, G. P. Purja Pun, R. Banerjee, K. N. Solanki, Y. Mishin, L. J. Kecskes, and K. A. Darling: Effect of Ta solute concentration on the microstructural evolution in immiscible Cu-Ta alloys, JOM 67, pp. 2802-2809 (2015).

R. K. Koju, K. A. Darling, L. J. Kecskes and Y. Mishin: Zener pinning of grain boundaries and structural stability of immiscible alloys, JOM 68, pp. 1596-1604 (2016).

M. Rajagopalan, K. A. Darling, S. A. Turnage, B. C. Hornbuckle, R. K. Koju, Y. Mishin, K. N. Solanki: Microstructural evolution in a nanocrystalline Cu-Ta alloy: A combined in-situ TEM and atomistic study, Materials & Design 113, 178-185 (2017).

R. K. Koju, K. A. Darling, K. N. Solanki and Y. Mishin: Atomistic modeling of capillary-driven grain boundary motion in Cu-Ta alloys, Acta Materialia, 148, 311-39119 (2018).

The results have also been reported in the TMS presentations:

R. K. Koju, K. A. Darling, L. J. Kecskes and Y. Mishin: Zener pinning of grain boundary migration in nanocrystalline immiscible alloys. TMS 2016 Annual Meeting and Exhibition February 14-18, Nashville, TN, February 17, 2016. [Invited presentation].

Raj K. Koju, K. A. Darling, L. J. Kecskes, Y. Mishin: Interaction of grain boundaries with nano-clusters in immiscible alloys, Symposium “Deformation and Transitions at Grain Boundaries V”, TMS 2017 Annual Meeting and Exhibition, February 26 – March 2, 2017, San Diego, California [Invited presentation].

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** Work on this project is conducted in close collaboration wth ARL. Atomistic simulations performed at GMU guide the experimental studies at ARL and at two other experimental groups (UNT and ASU). At the same time, the modeling and simulation work at GMU is driven by the goal of explaining and better understanding the experimental observations. The collaboration with the experimental groups also allow us to focus on models and situations that are most relevant to experimental conditions and technological applications. Most of our publications are co-authored with ARL collaborators, some with UNT and ASU collaborators. The collaboration with ARL keeps our work aligned with the Army missions.

The following patent application remains pending:

“Metallic Systems with Designed Architecture for Structural Stability and Elevated Temperatures, and Method of Making the Same”, Inventors: L. J. Kecskes, K. A. Darling, R. S. Mishra, K. N. Solanki, Y. Mishin, and M. Rajagopalan. The disclosure is under review at ARL.

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**Authors:** Tanaporn Rojhirunsakool, Kristopher A. Darling, Mark A. Tschopp, Ganga P. Purja Pun, Yuri Mishin and
**Keywords:** Immiscible alloys
**Abstract:** The formation of a metastable Cu–Ta solid solution in a mechanically alloyed Cu–10 at.%Ta alloy and its subsequent decomposition during annealing was investigated by atom probe tomography. During annealing, the as-milled Cu-rich alloy undergoes phase separation; Ta atoms diffuse out of the Cu lattice to form Ta clusters and particles along grain boundaries and within the Cu grains. The role of the Ta clusters and the nature of the solid solution as a potential strengthening mechanism for these alloys are discussed.
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**Authors:** G. P. Purja Pun, K. A. Darling, L. J. Kecskes and Y. Mishin
**Keywords:** Interatomic potential; atomistic simulation; immiscible alloys; Cu-Ta system; grain boundaries
**Abstract:** Atomistic computer simulations are capable of providing insights into physical mechanisms responsible for the extraordinary structural stability and strength of immiscible Cu-Ta alloys. To enable reliable simulations of these alloys, we have developed an angular-dependent potential (ADP) for the Cu-Ta system by fitting to a large database of first-principles and experimental data. This, in turn, required the development of a new ADP potential for elemental Ta, which accurately reproduces a wide range of properties of Ta and is transferable to severely deformed states and diverse atomic environments. The new Cu-Ta potential is applied for studying the kinetics of grain growth in nano-crystalline Cu-Ta alloys with different chemical compositions. Ta atoms form nanometer-scale clusters preferentially located at grain boundaries (GBs) and triple junctions. These clusters pin some of the GBs in place and cause a drastic decrease in grain growth by the Zener pinning mechanism. The results o
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**Article Title:** Atomistic modeling of capillary-driven grain boundary motion in Cu-Ta alloys
**Authors:** R.K. Koju, K.A. Darling, K.N. Solanki, Y. Mishin
**Keywords:** Atomistic modeling, Grain boundary, Zener pinning, Cluster precipitation
**Abstract:** Nanocrystalline Cu-Ta alloys are emerging as a new class of structural materials preserving the nano-scale 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 so- lution 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 GBecluster 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 nano- crystalline materials. Both the impingement of a moving GB on a set of Ta cl
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# Final Report

## Stabilization and strengthening of nanocrystalline materials by alloying

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**AWARD FROM THE U.S. ARMY RESEARCH OFFICE**

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# 1 Background and motivation

Many beneficial properties of nanocrystalline materials owe their origin to the large specific area (per unit volume) of grain boundaries (**GB**s) 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, the process known as the Hall-Petch mechanism. The Hall-Petch equation [1] predicts an increase in strength as the grains become smaller. It is known, however, that this equation is not followed at small grain sizes [2, 3]. Below a certain grain size, the strength stops to increase. This happens primarily because the dislocation sources inside the grains cease to operate and the dislocation pileups can no longer form. Instead, the plastic deformation is predominantly controlled by GB processes such as GB sliding and grain rotation [2–11].

Wider applications of nanocrystalline materials are hampered by the onset of grain growth at elevated temperatures. In some of the nanocrystalline materials, substantial grain growth can already occur at room temperature. The grain growth results in deterioration of the superior properties of nano-materials. The driving force for the grain growth has the 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.

In addition to temperature, the grain growth can also be caused by application of shear stresses [12–20]. The mechanism of the stress-induced grain growth is related to the shear-coupling effect [21–26] wherein a shear stress applied parallel to a GB causes its motion in the normal direction; inversely, GB motion driven by any force causes grain translations parallel to the GB plane [5, 21, 23]. For curved GBs, applied shear stresses create a driving force

for grain rotation; inversely, grain rotation creates a driving force for GB motion. For example, stress-induced grain growth in nanocrystalline Cu was observed in indentation creep experiments at room temperature and even at cryogenic temperatures [20]. Prevention of stress-driven GB motion is important for stabilization of nanocrystalline materials intended for service under mechanical loads. Even if the material is not prone to grain coarsening under stress-free conditions, the loads applied during the service can trigger grain growth and degrade the mechanical strength.

Whether the GB motion is caused by capillary forces or applied stresses, one of the most critical problems in the field of nanocrystalline materials is finding ways to stabilize the material's structure against grain growth.

Several approaches have been proposed for reducing 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 $\gamma$ by solute segregation [27–40]. Since the capillary driving force is proportional to $\gamma$, 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 [28, 29, 31, 33, 37–39, 41–43]. Several candidate systems have been identified as possible stable or metastable nanocrystalline alloys [29, 31, 37–39]. Some of them do display a high degree of structural stability in experiments, even though the exact thermodynamic nature of such alloys (stable, metastable or unstable) cannot be determined unambiguously. The *kinetic stabilization* is achieved by the reduction in GB mobility by the solute drag effect [40, 44–46] or by Zener pinning of GBs by small precipitates of a second phase [40, 46–52].

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. Nevertheless, the pursuit of a better fundamental understanding of each factor separately is a meaningful first step towards the development of more general stabilization models in the future. Such models will permit predictions and ultimately control of the grain size, which would pave the way for a rational design of highly stable nano-structural systems for diverse applications.

This project was focused on the kinetically stabilized Cu-Ta alloys. Nanocrystalline Cu-Ta alloys have recently attracted much attention due to their extraordinary structural stability and strength at high temperatures [35, 52–58]. 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, which are initially coherent with the Cu matrix (Fig. 1). These clusters strongly pin the GBs by the Zener mechanism, preventing grain growth. As a result, a Cu-Ta alloy can preserve the grain size of about 50-100 nm at high temperatures up to the melting point of Cu. The discovery of this fully stabilized nano-structure has opened 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 high strength (above 1 GPa) and small strain-rate sensitivity under tension and compression [55], lack of superplastic behavior, and excellent creep resistance [59]. While the exact mechanisms responsible for the high strength remain largely unknown, it can be assumed

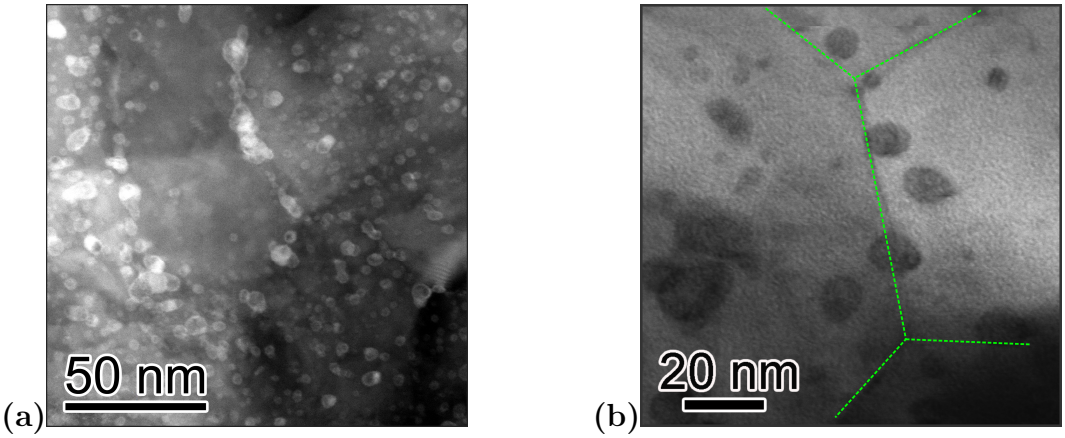


Figure 1: High resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of a Cu-3at.%Ta alloy consolidated by equal channel angular extrusion at 700 °C. The Ta clusters are revealed by Z-contrast. The average Cu grain size is about 86 nm. (a) Typical grain 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.

that the formation of dislocation pileups [1] is one of them. The Ta clusters residing at GBs can block the dislocation transmission and enhance the Hall–Petch mechanism [1]. The clusters located inside the grains can also contribute to the strength by restraining the dislocation glide and twinning. In addition, the GB clusters can create obstacles to the operation of GB deformation mechanisms by suppressing GB sliding and grain rotation. Further research is needed to confirm the operation of these mechanisms and evaluate their relative importance.

Cu-Ta alloys 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 GBs and separated by large areas of pure Cu boundaries. Since the clusters only occupy a small fraction of the total GB area, 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 [47–51]. 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 atomistic simulations [52] 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 consistent with the Zener model [47–51]. The GB migration was driven by an applied shear stress causing the GB motion due to the shear-coupling effect [21, 23]. It was noted that the applied stresses driving the GB motion were rather large and the speeds of GB migration were higher than the typical speeds under experimental conditions.

Little atomistic simulation work has been done so far on the effect of GB segregation

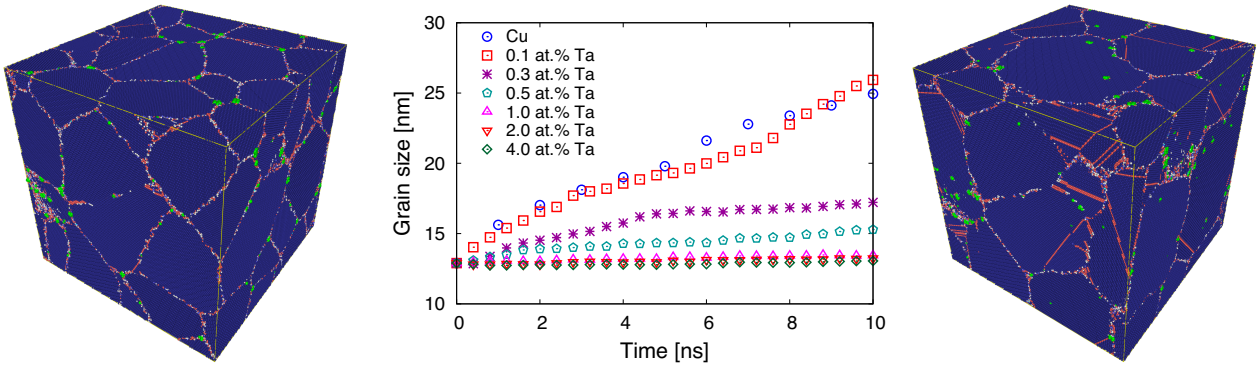


Figure 2: Atomistic simulations of grain stability in nano-crystalline Cu-Ta alloys [56]. The graph shows the grain size as a function of time, depending on the chemical composition of the alloy. The Ta clusters (green) initially precipitate at GBs and triple junctions. They pin the GBs and nearly stop the grain growth. In this example (0.3 at.%Ta, temperature 1200 K), the average grain size only increases from 13 nm (left) to 17 nm (right) over a 10 ns time period. In the process, some of the Ta clusters slightly coarsen by GB diffusion.

on grain stability of nanocrystals. Millett *et al.* [60] applied MD simulations to study the effect of oversized dopants on the excess GB energy. It was found that the latter could be reduced to zero at a certain level of segregation. The atomic interactions were described in a simplistic manner using a Lennard-Jones potential. The distribution of the dopant atoms between the GBs and the grains did not represent thermodynamic equilibrium. Most importantly, the authors only computed the excess GB energy, which does not have the same thermodynamic significance as the true GB *free* energy $\gamma$ entering all thermodynamic theories and controlling the grain stability.

# 2 Accomplishments under the current support

***Cu-Ta interatomic potential.*** An accurate and reliable interatomic potential has been constructed for the Cu-Ta system [56]. The Cu-Cu interactions were modeled with a well-tested embedded-atom method (EAM) potential developed previously [61]. For Ta-Ta interactions, a new potential has been developed using the angular-dependent potential (**ADP**) format [56, 62–66]. This potential format captures the angular-dependent component of interatomic bonding due to d-electrons and is more appropriate for BCC transition metals than EAM. The Cu-Ta cross-interactions were, likewise, described in the ADP format. The potential parameters were optimized using a large database of experimental properties and the results of first-principles density-functional theory (**DFT**) calculations. Extensive tests have shown that the Ta potential accurately reproduces a wide range of equilibrium properties of BCC Ta and is transferable to severely deformed states and many atomic environments different from the equilibrium BCC structure. For example, the melting temperature of Ta is predicted within a few degrees of the experimental value. The binary Cu-Ta potential reproduces the DFT energies of a large set of imaginary Cu-Ta in-

termetallic compounds that do not exist on the phase diagram but probe various atomic environments of the Cu and Ta atoms for different chemical compositions. The development of the new potentials has enabled us to perform accurate large-scale atomistic simulations and quantitative predictions of thermodynamic, kinetic and mechanical properties of Cu-Ta alloys.

***Tantalum nano-clusters.*** A combination of computer simulations with experiments conducted by collaborators has led to an understanding of the critical role of Ta clusters in the stabilization and strengthening of Cu-Ta alloys [35, 52–54, 56–58]. The simulations were performed by MD and Monte Carlo methods while the experiments utilized a number of characterization methods such as atom probe tomography (APT), scanning electron microscopy (SEM), transmission electron microscopy (TEM) (including high-resolution TEM), STEM, and other techniques. It was established that Ta clusters precipitate from the unstable solid solution during the thermal treatment following the high-energy cryogenic mechanical alloying (Fig. 1). The clusters were found to reside at GBs and pin them in place, leading to the structural stability of the material at high temperatures (Fig. 2).

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 or coalescence at high temperatures. The average cluster size and size distribution vary only slightly with temperature and chemical composition of the alloy. Adding more Ta mainly results in the formation of new clusters with nearly the same average size. The physical origin of this remarkable behavior of Ta atoms in Cu is not well understood. Previous simulations have shown that Ta and Cu form a thermodynamically stable nano-colloidal structure in the liquid state [67], with the Ta cluster size comparable to that in the solid state. The tendency to preserve the cluster size is likely to be related to a unique structure and energetics of Cu-Ta interfaces. It was suggested [67] 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 [67]. More research is needed to better understand this unusual effect on the atomic level and explore its existence in other immiscible systems.

Atomistic simulations and *in situ* TEM investigations have demonstrated that local structural changes at the interfaces between the Ta clusters and the Cu matrix have a profound effect on thermo-mechanical properties of Cu-Ta alloys. It was shown that the lattice misfit between the Ta clusters and the matrix decreases monotonically with temperature, promoting better coherency [58] (Fig. 3). The change in the misfit strongly correlates with the flow stress, which decreases with temperature but remains significantly higher than in other nanocrystalline materials. For example, the yield strength of the Cu-10at.%Ta alloy reaches nearly 1.4 GPa at room temperature and 0.75 GPa at 400°C.

***Effect of Ta clusters on grain boundary mobility.*** The dynamics of stress-driven and curvature-driven GB motion in Cu-Ta alloys has been investigated by systematic MD simulations. A large set of individual GBs was subject to an applied shear stress [52]. The stress gave rise to a driving force for GB migration caused by the shear-coupling effect [21–26]. By increasing the number of Ta clusters, the strength of pinning could be gradually ramped up until the GB was no longer able to overcome the pinning pressure and stopped. The shear-stress behavior during the GB–cluster interactions revealed two stages of the

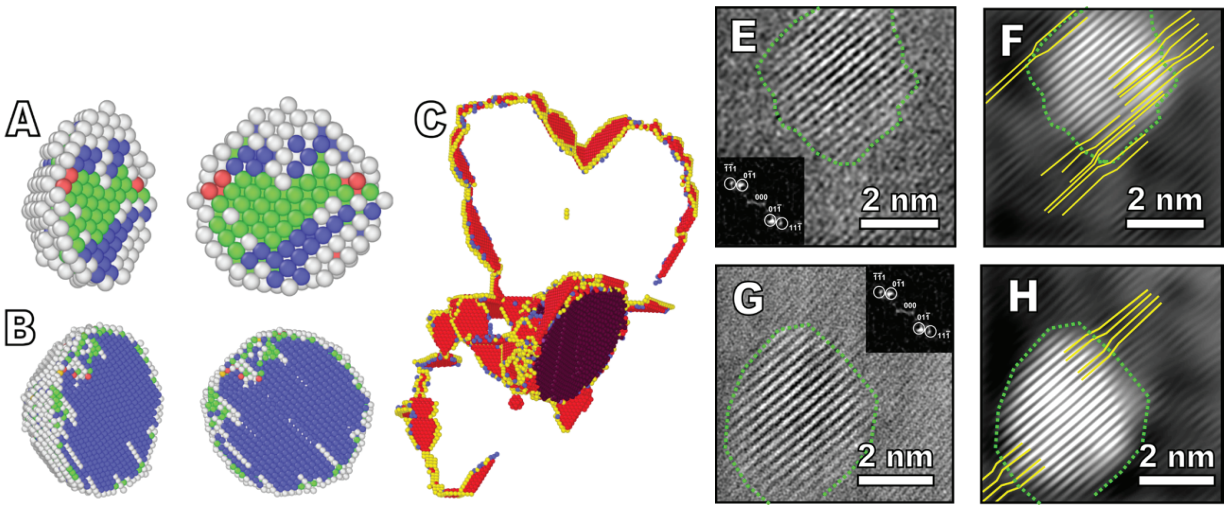


Figure 3: *Left:* Selected results of MD simulations of Ta clusters in Cu-Ta alloys, showing cross-sections of Ta clusters with diameters (A) 3 nm and (B) 7 nm at 426 °C. Ta atoms in FCC and BCC environments are shown in green and blue, respectively. The grey atoms represent other structural environments; (C) dislocation loops emitted by a Ta particle with a diameter of 7 nm at 426 °C. Note the dislocation splitting into partials separated by a stacking fault (red color). The FCC Cu atoms were removed for clarity and half of the Ta particle was cut out to reveal its spherical cross-section [58]. *Right:* TEM characterization of nanocrystalline Cu-10at.% Ta alloy, showing inverse Fourier filtered images of (E–F) coherent (3.47 nm in diameter) and (G–H) semi-coherent Ta nano-cluster (4.11 nm in diameter). The interfaces between the Ta clusters and Cu matrix are highlighted by dashed green lines. Insets in (E–H): indexed SAED patterns confirming nano-crystallinity [58].

process: attraction when the GB approached the clusters and retardation when it was trying to unpin from the clusters but was pulled back by the pinning force. This attraction-retardation behavior of the stress is illustrated in Fig. 4 and is exactly what is expected from the Zener model of GB pinning by spherical obstacles. To make a quantitative comparison with the Zener model, the latter was applied to back-calculate the GB free energy $\gamma$ from the simulation results. This was done for several alloy compositions and systems sizes, so that the number of clusters in the GB plane was varied by more than an order of magnitude. The values of $\gamma$ obtained remained always the same and matched the results of independent direct calculations. This excellent consistency of the results, as well as other tests conducted in [52], suggested that the suppression of GB mobility in Cu-Ta alloys could be accurately described by the Zener model.

In the stress-driven simulations [52], the applied shear stresses driving the GB motion were rather large and the speeds of GB migration were higher than normally observed under real conditions. While such simulations were relevant to shock deformation, it was not obvious that the conclusions would remain valid for grain growth under normal conditions. To address this question, the previous work [52] was extended to the motion of GBs under capillary forces whose magnitude was similar to that in real nanocrystalline materials during

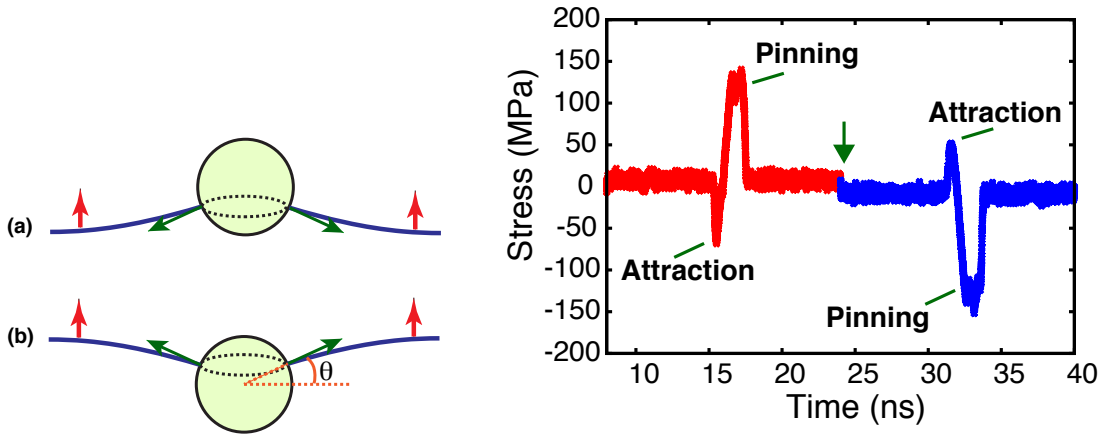


Figure 4: *Left:* Interaction of a moving GB with a spherical obstacle in the Zener model of pinning. (a) The boundary moving up comes in contact with the obstacle. The GB tension (shown by green arrows) is pulling the GB towards the obstacle, creating an attractive force. (b) The boundary is trying to break away from the obstacle and move on. The capillary force is now pulling the boundary back, creating a pinning pressure. The vertical red arrows indicate the direction of GB motion. *Right:* MD simulations of a GB interacting with Ta clusters in a Cu-0.027at.%Ta alloy at 900 K [52]. The plot shows the time dependence of the shear stress as the GB passes through a set of Ta clusters twice: forward (red) and backward (blue). The arrow shows the point of reversal of the GB motion. The stress profile is in close agreement with the Zener model of GB pinning.

grain growth. Since this part of the work has not been published,* it will be presented in more detail. An isolated cylindrical grain was created as a simple model. Although this idealized grain geometry ignores the triple lines and other constraints existing in real polycrystalline materials, it is perfect for studying the dynamics and mechanisms of curvature-driven GB motion *per se*.

Previous studies of the cylindrical grain in pure Cu [5] have shown that the grain shrinks and simultaneously rotates towards larger misorientation angles relative to the surrounding grain (matrix). The dynamics of this process was found to agree with predictions of the shear-coupling theory [5, 23]. In Cu-Ta alloys, two types of spatial distribution of Ta clusters relative to the GB were studied. In the first case, Ta clusters were created directly in the GB by composition-controlled semi-grand canonical Monte Carlo simulations. When the number of clusters was small, the capillary force could easily unpin the GB from the clusters and the grain continued to shrink and rotate in the pure Cu region of the simulation cell. The kinetics of this shrinkage process followed the same parabolic law as it did in the pure Cu simulations [5]. As the number of GB clusters increased, the GB took a longer time to unpin, until at a critical number of clusters it was unable to unpin on the simulation timescale. This resulted in total GB arrest. It is this arrest that leads to the suppression of grain growth in nanocrystalline Cu-Ta alloys.

In the second type of simulations, a set of Ta clusters was created within a concentric cylindrical shell inside the grain. This shell mimicked a cluster distribution left behind by

*A paper describing these results has been submitted for publication in Acta Materialia.

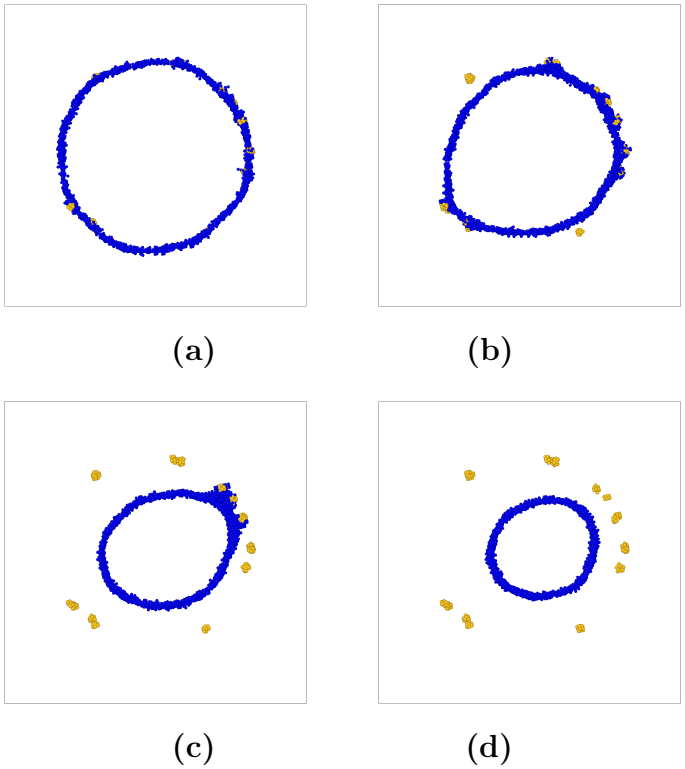


Figure 5: The unzipping mechanism of GB unpinning from Ta clusters in the Cu-0.05%Ta alloy at 900 K. (a) Ta clusters (yellow) are initially located at the GB (blue). (b) The GB has unpinned from 2 clusters and the unpinning process propagates along the GB. (c) The GB has unpinned from most of the clusters. (d) The GB has totally unpinned from the clusters. FCC Cu atoms are not shown for clarity.

an imaginary smaller grain that used to be pinned but was able to detach from the clusters and migrated elsewhere. The goal was to study the GB interaction with this set of intragranular clusters as the GB shrunk by capillary forces. As in the previous case, several temperatures and alloy compositions were studied. The results were similar to the previous case, confirming that our conclusions do not depend on the initial conditions. In particular, the number of clusters causing the GB arrest was again fully consistent with the Zener model. Furthermore, in both cases the unpinning process followed the unzip mechanism illustrated in Fig. 5. The GB initially unpins from one random cluster and the free GB segment 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.

To better understand the cluster nucleation process, the simulations were extended to disordered Cu-Ta solid solutions representing the state of the material after the mechanical alloying and prior to the thermal treatment. The randomly distributed Ta atoms inserted in the Cu matrix imposed a drag force that reduced the rate of GB migration and grain rotation in comparison with pure Cu. However, this drag effect was not nearly as strong as the pinning effect of the clusters. Much higher Ta concentrations were required to achieve the same level of retardation or stop the GB motion.

An interesting feature of GB migration in the random Cu-Ta alloy is the stop-and-go character manifested in the stepwise shape of the area-time curves (Fig. 6). This stop-and-go

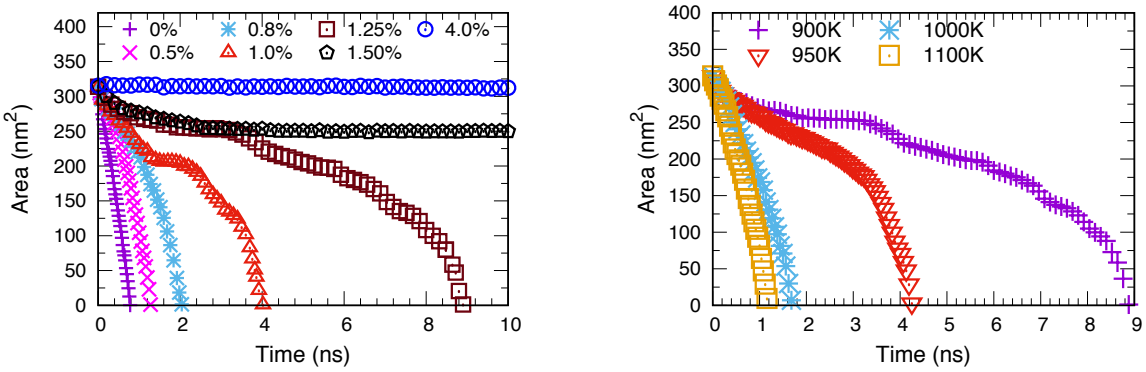


Figure 6: Grain area as a function of time in MD simulations of random Cu-Ta solutions. The alloy compositions (at.%Ta) at 900 K (left) and temperatures of the 1.25at.%Ta alloy (right) are indicated in the legends. Note the steps representing the stop-and-go mode of GB motion at low temperatures and/or high Ta concentrations.

behavior is especially pronounced at higher Ta concentrations and/or lower temperatures. 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 results, 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 [68], the Portevin – Le Chatelier effect [69], and other cases of stick-slip behavior. These simulations show that the precipitation of Ta clusters from the unstable solid solution occurs predominantly by heterogeneous nucleation at GBs.

The process just described creates an array of Ta clusters behind a moving GB. Such clusters can continue to grow until they reach the optimal size. Some of them eventually stop the motion of other moving boundaries and become GB clusters, while others still remain inside the grains. The existence of Ta clusters inside the grains has been well documented in recent experiments [35, 54, 55, 57, 58] (Fig. 1) and is one of the contributors to the high strength and creep resistance [59] of Cu-Ta alloys.

***Mechanical properties of Cu-Ta alloys.*** Atomistic simulations of uniaxial tensile and compressive deformation have been performed at various temperatures, alloy compositions and strain rates. Load-controlled tensile tests have shown that the formation of Ta clusters in nanocrystalline Cu results in a drastic increase in the yield stress and ultimate strength in comparison with pure Cu [53]. For example, a Cu-6.5at.%Ta alloy annealed at 700 K for cluster precipitation shows the yield stress of 1.5 GPa, which is close to the experimental value of 1.4 GPa [55]. More systematic computational tests were performed for compressive deformation (to be published). Equilibrium distribution of 4 at.%Ta was created in nanocrystalline Cu by Monte Carlo simulations and, as expected, was found to

have the form of nano-clusters residing predominantly at GBs. Uniaxial compression was carried out with several strain rates at two temperatures. The flow stresses were found to be close to the results of experimental tests performed on the same material and higher than the flow stress of nanocrystalline Cu with the same grain size (Fig. **??**).

The slopes of the stress versus strain rate curves in Fig. **??** show that the strain rate sensitivity increases with temperature, a trend which was also found in experiments. For a quantitative comparison, the strain-rate sensitivity parameter $m$ was computed from the simulation results. The values obtained, $m = 0.029 \pm 0.004$ at 300 K and $m = 0.075 \pm 0.004$ at 1000 K, were close to the experimental numbers. Examination of microstructures before and after the deformation did not reveal any significant changes in the grain size, pointing to high structural stability. By contrast, similar deformation tests performed on nanocrystalline Cu (same initial grain size) resulted in significant grain growth and larger strain-rate sensitivity. Furthermore, Fig. **??** demonstrates that the GB sliding and grain rotation processes occurring during the deformation are less pronounced in the Cu-Ta alloy than in pure Cu. Such processes constitute the basic mechanisms of superplastic deformation. The suppression of these processes by Ta clusters explains the absence of superplastic behavior in nanocrystalline Cu-Ta alloys even at temperatures as high as 80% of the melting point discovered in recent experiments.

# 3 Publications and presentations

Results of this project have been reported in the following publications:

1. Tanaporn Rojhirunsakool, Kristopher A. Darling, Mark A. Tschopp, Ganga P. Purja Pun, Yuri Mishin and Laszlo J. Kecskes: Structure and thermal decomposition of a nanocrystalline mechanically alloyed supersaturated Cu–Ta solid solution, *MRS Communications* **5**, pp. 333-339 (2015).

2. G. P. Purja Pun, K. A. Darling, L. J. Kecskes and Y. Mishin: Angular-dependent interatomic potential for the Cu-Ta system and its application to structural stability of nano-crystalline alloys, *Acta Materialia*, **100**, 377-391 (2015).

3. B. C. Hornbuckle, T. Rojhirunsakool, M. Rajagopalan, T. Alam, G. P. Purja Pun, R. Banerjee, K. N. Solanki, Y. Mishin, L. J. Kecskes, and K. A. Darling: Effect of Ta solute concentration on the microstructural evolution in immiscible Cu-Ta alloys, *JOM* **67**, pp. 2802-2809 (2015).

4. R. K. Koju, K. A. Darling, L. J. Kecskes and Y. Mishin: Zener pinning of grain boundaries and structural stability of immiscible alloys, *JOM* **68**, pp. 1596-1604 (2016).

5. M. Rajagopalan, K. A. Darling, S. A. Turnage, B. C. Hornbuckle, R. K. Koju, Y. Mishin, K. N. Solanki: Microstructural evolution in a nanocrystalline Cu-Ta alloy: A combined in-situ TEM and atomistic study, *Materials & Design* **113**, 178-185 (2017).

6. R. K. Koju, K. A. Darling, K. N. Solanki and Y. Mishin: Atomistic modeling of capillary-driven grain boundary motion in Cu-Ta alloys, *Acta Materialia*, **148**, 311-39119 (2018).

The results have also been reported in the TMS presentations:

R. K. Koju, K. A. Darling, L. J. Kecskes and Y. Mishin: Zener pinning of grain boundary migration in nanocrystalline immiscible alloys. TMS 2016 Annual Meeting and Exhibition February 14-18, Nashville, TN, February 17, 2016. [Invited presentation].

Raj K. Koju, K. A. Darling, L. J. Kecskes, Y. Mishin, "Interaction of grain boundaries with nano-clusters in immiscible alloys", Symposium "Deformation and Transitions at Grain Boundaries V", TMS 2017 Annual Meeting and Exhibition, February 26 – March 2, 2017, San Diego, California [Invited presentation].

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