Angular-dependent interatomic potential for the Cu–Ta system and its application to structural stability of nano-crystalline alloys

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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 of the simulations are well consistent with experimental observations and suggest possible mechanisms of the stabilization effect of Ta.

1. Introduction

Recent years have seen a rapidly growing interest in immiscible metallic alloys due to their favorable combination of high mechanical strength and extraordinary stability at high temperatures [1–11]. The improved thermal stability is especially important for nano-crystalline alloys, which are characterized by a strong tendency for rapid grain growth at elevated temperatures. In particular, Cu–Ta has emerged as one of the most promising immiscible alloy systems for high-temperature, high-strength applications [8,10,9,7]. Cu and Ta have different crystalline structures (FCC and BCC, respectively) and negligible mutual solubility in the solid state [12]. High-energy mechanical alloying is capable of forcing a significant amount of Ta into a metastable FCC solid solution with Cu [8,7]. During subsequent thermal processing, Ta precipitates in a variety of structural forms ranging from atomic-level coherent clusters to incoherent particles reaching a few nanometers and larger in size.

It is the formation of the Ta clusters that is believed to be responsible for the extraordinary properties of the mechanically alloyed Cu–Ta alloys. Such clusters tend to form at grain boundaries (GBs), pinning them by the Zener mechanism [13] and preventing grain growth even in nano-crystalline alloys with a strong capillary driving force for coarsening. In addition, the clusters themselves contribute to the strengthening of the material, making it significantly stronger than predicted by the Hall–Petch model of GB hardening [14,15]. While the exact mechanisms of these effects remain the subject of active current research, it is likely that the nanometer and sub-nanometer size clusters restrain dislocation glide in the Cu lattice similar to the Guinier–Preston zones [16,17] in Al(Cu) alloys. Furthermore, the cluster located at GBs are likely to increase the resistance to GB sliding, which is one of the important deformation and accommodation mechanisms in nano-grained materials [18].

Atomistic computer simulations offer a powerful tool for gaining deeper insights into the physical mechanisms of the Ta effect. Such simulations typically employ the molecular dynamics (MD) and Monte Carlo (MC) methods and rely on semi-empirical interatomic potentials to describe atomic interactions [19]. Our previous simulations of the Cu–Ta system [7] utilized an interatomic potential [20] that had been developed with emphasis on surface phenomena, such as wetting and dewetting of Cu thin films deposited on Ta substrates. While this potential does capture basic trends in this system, quantitative investigations of immiscible bulk alloys require a more accurate potential developed for a wider range of applications. Indeed, since the development of the previous potential [20], more first-principles data became available and potential generation and testing methods have been significantly improved. The goal of this work is to develop a new and
improved Cu–Ta potential taking advantage of the richer first-principles databases and more advanced fitting and testing methodologies existing today.

The strategy for achieving this goal is as follows. We will adopt the existing embedded-atom method (EAM) [21] potential for Cu [22], which has been successfully tested in many materials applications. A new potential will be constructed for Ta. The previously developed angular-dependent potential (ADP) [23] had a flaw: due to an error in the fitting program, some of the elastic constants of Ta are different from those reported in the paper. In addition, the melting temperature of Ta predicted by that potential is significantly higher than experimental. Several other potentials have been developed for Ta [24–28], the most recent ones being the EAM potentials by Li et al. [27] and Ravelo et al. [29]. The Ravelo EAM potential [29] is especially accurate and transferable as will be discussed below. However, we prefer the ADP potential format [30,23,20,31,32], which we believe to be more appropriate for BCC transition metals than the regular EAM. We therefore set the goal of constructing a new ADP potential for Ta, and along the way to improve on some of the properties of the Ravelo potential [29], such as the melting temperature, the surface energies and the interstitial formation energies.

The development of the ADP Ta potential will be described in Sections 2 and 3 and the testing results will be reported in Section 4. We compare the predictions of the new potential with first-principles calculations and the potentials by Li et al. [27] and Ravelo et al. [29]. Having a Ta potential, we then cross it with EAM Cu [22] by fitting the mixed-interaction functions in the ADP format. The fitting and testing results for the binary Cu–Ta potential are presented in Section 5. The ability of the new potential to model the Cu–Ta system is demonstrated in Section 6 by studying structural stability of nano-crystalline Cu–Ta alloys. Two types of alloys are tested, one modeling the highly non-equilibrium state with a random dispersion of Ta atoms created by mechanical alloying, and the other mimicking the heat-treated alloys containing Ta clusters. The results of this study are well consistent with experimental observations and reveal some interesting effects such as the strong pinning of GBs by the Ta clusters and the formation and growth of Ta clusters in random alloys by the mechanism of GB diffusion.

2. Potential Format

In the ADP formalism [30,23,20,31,32], the total energy of a system is expressed by

\[ E_{\text{tot}} = \frac{1}{\rho} \sum_{(ij) \neq \rho} \Phi_{\rho} (\mathbf{r}_i) + \sum_{\text{f}} F_{\text{f}} (\rho_i) + \frac{1}{2} \sum_{i \neq j} (\rho_i^2)^2 + \frac{1}{2} \sum_{i \neq j} (\rho_i^4)^2 - \frac{1}{6} \sum_{i \neq j} \mathbf{v}^2, \]  

(1)

where indices \( i \) and \( j \) enumerate atoms and superscripts \( \alpha, \beta = 1, 2, 3 \) represent Cartesian components of vectors and tensors. In Eq. (1), \( \Phi_{\rho} (\mathbf{r}_i) \) is the pair interaction energy between an atom \( i \) of chemical species \( s_i \) located at position \( \mathbf{r}_i \) and an atom \( j \) of chemical species \( s_j \) located at position \( \mathbf{r}_j = \mathbf{r}_i + \mathbf{r}_j \). The second term is the energy of embedding an atom of chemical species \( s_i \) in the host electron density \( \rho_i \) induced at site \( i \) by all other atoms. The host electron density is given by

\[ \rho_i = \sum_{f=1} \rho_f (\mathbf{r}_i), \]  

(2)

where \( \rho_f (\mathbf{r}_i) \) is the atomic electron density function of a neighboring atom \( f \) of chemical species \( s_j \). The first two terms in Eq. (1) constitute the standard embedded-atom method (EAM) format [21].

The remaining terms in Eq. (1) represent the non-central character of bondings and include the dipole vectors

\[ \mu_f^2 = \sum_{j \neq i} \mathbf{u}_{s_j} (\mathbf{r}_j) \mathbf{r}_j^2, \]  

(3)

and quadrupole tensors

\[ \mathbf{x}_f^2 = \sum_{j \neq i} \mathbf{w}_{s_j} (\mathbf{r}_j) \mathbf{r}_j^2, \]  

(4)

where the trace of \( \mathbf{x}_f^2 \) is

\[ v_i = \sum_x \mathbf{x}_{i,x}^2, \]  

(5)

In these equations, \( u_{s_i} (\mathbf{r}) \) and \( w_{s_i} (\mathbf{r}) \) are additional potential functions of the radial distance between atoms. For the binary Cu–Ta system, the construction of an ADP potential requires 13 potential functions: \( \Phi_{\text{CuCu}} (\mathbf{r}) \), \( \Phi_{\text{TaTa}} (\mathbf{r}) \), \( \Phi_{\text{CuTa}} (\mathbf{r}) \), \( \rho_{\text{Cu}} (\mathbf{r}) \), \( \rho_{\text{Ta}} (\mathbf{r}) \), \( F_{\text{Cu}} (\mathbf{r}) \), \( F_{\text{Ta}} (\mathbf{r}) \), \( u_{\text{CuCu}} (\mathbf{r}) \), \( u_{\text{TaTa}} (\mathbf{r}) \), \( u_{\text{CuTa}} (\mathbf{r}) \), \( w_{\text{CuCu}} (\mathbf{r}) \), \( w_{\text{TaTa}} (\mathbf{r}) \), and \( w_{\text{CuTa}} (\mathbf{r}) \). In this work, the ADP potential functions for pure Ta will be constructed separately and then crossed with an existing EAM potential for pure Cu developed in [22] to obtain a binary potential.

3. Fitting of the ADP Potential for Ta

The pair-wise interaction function \( \Phi_{\text{TaTa}} (\mathbf{r}) \), the host electron density \( \rho_{\text{Ta}} (\mathbf{r}) \), and the quadrupole interaction function \( w_{\text{TaTa}} (\mathbf{r}) \) were represented by cubic splines. For each spline, not only the values of the function but also positions of the nodes were adjustable parameters. Each function was parameterized by five nodes, giving a total of 30 fitting parameters. To impose a smooth cutoff at a distance \( r_c \), the splines were multiplied by the truncation function \( \psi (r - r_c) / h \), were

\[ \psi (x) = \begin{cases} x^4 & \text{if } x < 0, \\ 0 & \text{if } x \geq 0. \end{cases} \]  

(6)

The truncation introduces two more parameters \( r_c \) and \( h \), bringing the total number of fitting parameters to 32. In this work, we did not use the dipole term. It was found that it did not improve the potential quality enough to warrant its inclusion.

The embedding energy \( F_{\text{Cu}} (\mathbf{r}) \) was obtained by inverting Eq. (1) to ensure that the energy \( E \) per atom of BCC Ta follows Rose’s equation of state postulated in the form

\[ E(a) = E_0 (1 + 2\alpha + f_2 a^2 + f_4 a^4) e^{-a}, \]  

(7)

where

\[ \alpha = \frac{a}{a_0} - 1, \]  

(8)

and

\[ a = \left( -\frac{9V_0 B}{E_0} \right)^{1/2}. \]  

(9)

Here, \( a \) is the cubic lattice parameter and \( E_0 \), \( a_0 \) and \( V_0 \) are the equilibrium values of the cohesive energy, lattice parameter and atomic volume, respectively. In Eq. (7), the coefficients \( f_2 \) and \( f_4 \) could also be treated as adjustable parameters. However, in this work we used the values \( f_2 = -0.035744 \) and \( f_4 = -0.020879 \) optimized by Ravelo and co-workers [29]. Note that this parameterization of the potential functions guarantees an exact fit to \( E_0 \), \( B \) and \( a_0 \).

The potential parameters were fitted to the elastic moduli, vacancy formation energy and energies of low index surfaces of BCC Ta and energies of several alternate crystalline structures of Ta. The parameters were optimized by minimizing the sum of weighted mean-squared deviations of computed properties from
the respective experimental and/or first-principles values. A two-step optimization process was applied. First, a preliminary optimization was implemented utilizing a genetic algorithm developed in our previous work [31], followed by a more refined fit using a simulated annealing method.

4. Testing results for the Ta potential

The optimized potential functions are plotted in Fig. 1. The pair potential and embedding energy function are plotted in the effective pair format [33,34], although the host electron density $\rho$ has not been scaled and the minimum of the embedding energy occurs at $\rho = 1.074599$.

Some of the properties of BCC Ta predicted by the potential are summarized in Table 1 in comparison with experimental data, first-principles calculations and predictions of EAM potentials [29,27]. All properties, except for the melting point, were computed at absolute zero temperature. For defect energies, the structures were relaxed and the results were tested for convergence with respect to the system size. The formation energies of vacancies ($E_{\text{v}}^f$) and interstitials ($E_{\text{i}}^f$) were computed for a set of different system sizes, plotted against the inverse of the number of atoms and extrapolated to the infinite size [35]. The vacancy migration energy $E_{\text{m}}^{\text{v}}$ was calculated in a periodic supercell containing 1024 atoms using the nudge elastic band (NEB) method [36,37]. The activation energy of self-diffusion was obtained by $Q = E_{\text{f}}^f + E_{\text{m}}^{\text{v}}$. The generalized stacking fault energies were computed in the gamma-surface mode [38]. Namely, two half-crystals were translated with respect to each other in a given direction parallel to a chosen crystal plane. After each increment of translation, the structure was relaxed with respect to atomic displacements in the $x$ direction normal to the fault plane while keeping the $y$ and $z$ components of atomic coordinates fixed. Most of the computations reported here used the LAMMPS simulation program [39].

Table 1 shows that the ADP potential accurately reproduces the elastic constants $c_{11}$ and $c_{12}$ but slightly overestimates $c_{44}$. Fig. 2 presents phonon dispersion relations for BCC Ta computed at 300 K by MD simulations [40] with the ADP potential. In this method, the dynamical matrix is reconstructed from correlations between atomic displacements and is subject to a Fourier transformation in high-symmetry directions in the reciprocal space. The simulations were performed in a periodic supercell containing $16 \times 16 \times 16$ primitive unit cells. The phonon dispersion curves are in qualitative agreement with experimental measurements by neutron scattering [41]. While low phonon frequencies are reproduced by the potential accurately, the maximum phonon frequency at point H of the zone boundary is underestimated while the frequencies at points P and N are overestimated. Similar deviations were found with other potentials. For example, the maximum frequency in the phonon density of states predicted by the present ADP potential and the two EAM potentials developed by Ravelo et al. [29] are, respectively, 5.05, 4.56 and 4.25 THz. The experimental value is 5.03 THz. Note that phonon frequencies were not included when fitting the potentials.

The vacancy migration energy predicted by the ADP potential (0.82 eV) overestimates the accepted experimental value of 0.7 eV but falls within the range of first-principles calculations. The activation energy of self-diffusion is consistent with experimental measurements and first-principles calculations. For interstitials, the potential underestimates the first-principles formation energy for the (100) dumbbell orientation, as do all other potentials [29,27]. However, the energies of the (110) and (111) interstitials are reproduced more accurately than with other potentials. The energy $\gamma_{\text{tw}}$ of the (211) twin boundary is in good agreement with the first-principles value (no experimental data is available). The energies $\gamma_{\text{i}}$ of low-index surfaces were included in the potential fit and are in good agreement with first-principles calculations. The ranking of the surface energies is also consistent with first-principles calculations:


Table 1

Properties of BCC Ta computed with the present ADP potential in comparison with experimental data, first-principles calculations and previously developed EAM potentials [29,27]. The properties marked by an asterisk were included in the potential fit. The values marked by a dagger were computed in this work using the published potentials.

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th>Ab initio</th>
<th>ADP</th>
<th>EAM$^\dagger$</th>
<th>EAM$^\ddagger$</th>
<th>EAM$^\S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å$^\S$)</td>
<td>3.0326$^a$; 3.3039$^b$</td>
<td>3.26$^c$; 3.3086$^d$</td>
<td>3.315$^e$; 3.3$^f$</td>
<td>3.27864$^g$; 3.311$^h$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_0$ (eV)$^*$</td>
<td>−8.1$^i$</td>
<td>194.2$^j$; 198$^j$</td>
<td>195.58$^k$; 194$^l$</td>
<td>190.95$^m$; 196$^m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>266.3$^n$; 266.0$^n$</td>
<td>265; 259.6$^o$; 258.7$^o$</td>
<td>249.68$^p$; 257$^p$</td>
<td>249.68$^q$; 257$^q$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{11}$ (GPa)$^*$</td>
<td>158.2$^r$ 160.94$^r$</td>
<td>159$^s$; 165.2$^t$; 168.8$^t$</td>
<td>161.59$^u$ 163$^u$</td>
<td>143.6$^v$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_{12}$ (GPa)$^*$</td>
<td>87.4$^w$; 82.47$^w$</td>
<td>74$^x$; 64.2$^y$; 67.8$^y$</td>
<td>70.26$^z$; 71$^z$</td>
<td>70.26$^{zz}$; 71$^{zz}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_f^i$ (eV)$^*$</td>
<td>2.2–3.1$^a$</td>
<td>2.91$^a$; 3.14$^a$</td>
<td>3.06</td>
<td>2.43</td>
<td>2.00</td>
<td>2.76</td>
</tr>
<tr>
<td>$E_{mc}$ (eV)</td>
<td>0.7$^a$</td>
<td>0.76$^a$; 0.83$^h$</td>
<td>0.82</td>
<td>0.99</td>
<td>1.08</td>
<td>1.24</td>
</tr>
<tr>
<td>$Q$ (eV)</td>
<td>3.8–4.39$^a$</td>
<td>3.98$^a$</td>
<td>3.8</td>
<td>3.42</td>
<td>3.08</td>
<td>4.00</td>
</tr>
<tr>
<td>$E_f^i$ (100) (eV)</td>
<td>7.00$^a$</td>
<td>5.86</td>
<td>5.34$^a$</td>
<td>5.89$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_f^i$ (110) (eV)</td>
<td>6.38$^a$</td>
<td>5.65</td>
<td>4.55$^a$</td>
<td>5.12$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_f^i$ (111) (eV)</td>
<td>5.83$^a$</td>
<td>5.62</td>
<td>4.44$^a$</td>
<td>5.05$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_m$ (K)</td>
<td>3293</td>
<td>3296</td>
<td>3033</td>
<td>3080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma_{sl}$ (J/m$^2$)</td>
<td>0.304$^a$</td>
<td>0.28</td>
<td>0.29$^a$</td>
<td>0.30$^a$</td>
<td>0.42$^a$</td>
<td></td>
</tr>
<tr>
<td>$\gamma_{fr}$ (J/m$^2$)</td>
<td>0.840$^a$</td>
<td>0.782</td>
<td>0.864</td>
<td>0.803</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110)/(111)</td>
<td>1.947$^a$</td>
<td>2.041</td>
<td>2.181$^a$</td>
<td>2.182$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110)/(110)</td>
<td>1.947$^a$</td>
<td>2.041</td>
<td>2.194</td>
<td>2.208</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(211)/(110)</td>
<td>4.079$^a$</td>
<td>3.927</td>
<td>3.422$^a$</td>
<td>3.312$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(211)/(111)</td>
<td>0.947$^a$</td>
<td>0.918</td>
<td>1.017</td>
<td>0.975</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. [29].
$^b$ Ref. [64].
$^c$ Ref. [23].
$^d$ Ref. [65].
$^e$ Ref. [66].
$^f$ Ref. [67].
$^g$ Refs. [68,69].
$^h$ Ref. [70].
$^i$ Ref. [71].
$^j$ Ref. [72].
$^k$ Ref. [73].
$^l$ Ref. [74].
$^m$ Ref. [75].
$^n$ Ref. [76].
$^o$ Ref. [77].
$^p$ Ref. [78].
$^q$ Ref. [79].
$^r$ Ref. [80].
$^s$ Ref. [81].
$^t$ Ref. [82].
$^u$ Ref. [83].
$^v$ Ref. [84].
$^w$ Ref. [27].

$\gamma_{(110)} < \gamma_{(100)} < \gamma_{(211)} < \gamma_{(111)}$. The EAM potentials [29,27] significantly underestimate the surface energies.

Generalized stacking faults energies for the (110) and (211) fault planes are displayed in Fig. 3. The first-principles gamma-surfaces [29,23] are shown for comparison. For the sake of completeness, we also include the earlier first-principles calculations by Frederiksen and Jacobsen [42] for the (111)/(110) fault, which are unrelated and thus predictably overestimate the recent relaxed calculations [29,23]. The maxima along the gamma surfaces represent unstable stacking fault energies $\gamma_{sl}$, which are summarized in Table 1. The ADP predictions are in excellent agreement with first-principles calculations, even though the latter were not included in the potential fit. Unstable stacking fault energies are important for simulations of core effects in dislocation glide.

Equilibrium energies $\Delta E$ of several alternate structures of Ta relative to the BCC ground state are summarized in Table 2. The agreement between the ADP energies and first-principles data is reasonable. To facilitate comparison with other potentials, we plot the energies predicted by the ADP and EAM potentials versus the first-principles data (Fig. 4). The bisecting line in this plot is the line of perfect agreement. Despite the scatter of the points, all potentials show a strong correlation with first-principles results. The
scatter is more significant for the potential by Li et al. [27]. The alternate structures were included in this analysis as a test of transferability of the potentials to various atomic environments different from the BCC structure. It is important to note that both the ADP and EAM potentials correctly predict the metastable \( b\)-\( U \) and \( b\)-\( W \) structures to be closest in energy to the BCC ground state.

The \( b\)-phase of Ta (\( b\)-\( U \) prototype) is often observed experimentally in deposited thin films [26,43,44]. The proposed ADP potential should be suitable for thin film simulations involving the \( b\)-phase.

We next discuss the performance of the potential under large structural distortions. The pressure–volume relation computed for BCC Ta at 0 K is in good agreement with experiment and first-principles calculations up to 1 TPa (Fig. 5). As a further test beyond the limits of linear elasticity, we performed a static uniaxial compression of BCC Ta at 0 K in three different directions. Stress–strain relations under such conditions are relevant to shock wave propagation and were computed by Ravelo et al. [29]. The material was compressed in a chosen \( x\)-direction up to \( \varepsilon = 40\% \) while keeping fixed dimensions in the \( y\) and \( z\) directions. The results are shown in Fig. 6 in comparison with first-principles calculations [29]. While marked deviations are observed under compressions exceeding 20%, the overall agreement with first-principles calculations is good and on the same level of accuracy as with the EAM potentials [29].

Several other tests were conducted to evaluate the transferability of the potential to highly distorted configurations. One of them involved homogeneous twinning and anti-twinning deformation paths, which are relevant to mechanical behavior of Ta. This deformation carries a BCC crystal back to itself but with a twinning or anti-twinning orientation relative to the initial state. A detailed crystallographic description of this path can be found in Ref. [23].

\[
\begin{align*}
\text{Fig. 2.} & \quad \text{Phonon dispersion relations for BCC Ta computed with the ADP potential at 300 K (solid lines). The circles (○) and triangles (▵) represent experimental data from Ref. [41].} \\
\text{Fig. 3.} & \quad \text{Cross-sections of gamma surfaces for BCC Ta computed with the present ADP potential in comparison with first principles (DFT) calculations (○, □, ◼, ◄, ◄, ◄): (a) (110)(100), (b) (110)(110), (c) (111)(111), (d) (110)(211), (e) (111)(211). The displacements are normalized by the period in the respective direction.}
\end{align*}
\]
The deformation is described by a shear parameter which is zero in the initial state and attains the values of $1/\sqrt{2}$ and $-\sqrt{2}$ for the twin and anti-twin orientations, respectively. The energy along this paths computed with the ADP potential is shown in Fig. 7 in comparison with first-principles calculations [23]. The potential accurately reproduces the maximum anti-twinnning energy (1.04 eV/atom) and slightly underestimates the maximum twinning energy (0.15 eV/atom).

The potential was also tested for three volume-conserving deformation paths: orthorhombic, tetragonal and trigonal. Orthorhombic deformation is implemented by elongation of the BCC cubic unit cell along the [001] direction with simultaneous compression along the [110] direction to preserve the equilibrium BCC volume. The respective deformation parameter $p$ was defined in [45]. For the tetragonal deformation path (Bain path), the unit cell is elongated in the [001] direction with simultaneous compression in the [100] and [010] directions by equal amounts. The deformation is measured by the parameter $p = c/a$ with $p = 1$ for the BCC structure and $p = \sqrt{2}$ for the FCC structure. Further elongation produces a local energy minimum corresponding to a body-centered tetragonal (BCT) structure. Finally, for the trigonal deformation we compress the BCC structure along the [111] axis with simultaneous elongation in perpendicular directions. The deformation parameter $p$ is the Lagrangian strain described in [46]. The deformation starts with $p = 0$ (BCC structure) and creates the simple cubic (SC) and FCC structures at $p = 2$ and $p = 4$, respectively. Comparison of the ADP and EAM potentials with first-principles potentials by Ravelo et al. [29] demonstrates about the same level of accuracy as the potentials by Li and co-workers [27]. The potential by Li and coworkers [27] is somewhat less accurate. In particular, for the tetragonal deformation path it predicts a local minimum of energy for the FCC structure instead of a maximum.

To evaluate thermal properties predicted by the ADP potential, the linear thermal expansion factor was computed as a function of temperature (Fig. 9). The simulations utilized a periodic cubic supercell containing 16000 atoms. MD simulations were executed in the NPT (fixed temperature and pressure) ensemble in which all three dimensions of the supercell were allowed to fluctuate independently to ensure zero components of pressure in all three directions. The cubic lattice parameter $a$ was averaged over a 1 ns long MD run and the linear expansion coefficient was defined as $(a - a_f)/a_f$, where $a_f$ is the lattice parameter at room temperature.
temperatures. The ADP potential demonstrates a good agreement with experimental data up to the temperature of 1200 K but underestimates the experimental lattice constant at higher temperatures. The melting temperature $T_m$ of BCC Ta was computed by two methods: the phase coexistence method and the interface velocity method. The phase coexistence method is described in detail elsewhere.

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The melting temperature $T_m$ of BCC Ta was computed by two methods: the phase coexistence method and the interface velocity method. The phase coexistence method is described in detail elsewhere.

where [47,48]. In short, a simulation block containing a plane solid–liquid interface is equilibrated by a micro-canonical MD simulation and the equilibrium temperature and pressure (defined here as the trace of the stress tensor averaged over the system) are calculated. The simulation is repeated several times starting...

**Fig. 6.** Stress components as functions of strain during uniaxial compression of BCC Ta calculated with the present ADP potential in comparison with first-principles (DFT) calculations [29]. Crystallographic directions: (a) $x:[100], y:[010], z:[001]$, (b) $x:[110], y:[110], z:[001]$, (c) $x:[111], y:[110], z:[112]$.

**Fig. 7.** Energy along the homogeneous twinning and anti-twinning deformation paths in BCC Ta calculated with the present ADP potential in comparison with first-principles (DFT) calculations [23].

**Fig. 8.** Energy along three homogeneous deformation paths of Ta computed with interatomic potentials in comparison with first-principles (DFT) calculations [45]. (a) Orthorhombic deformation path. (b) Tetragonal deformation path. (c) Trigonal deformation path. Potentials: EAM1 [29], EAM2 [29], EAM3 [27] and ADP (present work). For each deformation path, the volume remains fixed at its equilibrium value in BCC Ta.

**Fig. 9.** Linear thermal expansion factor (%) of BCC Ta relative to room temperature computed with the present ADP potential in comparison with experimental data [89]. The experimental melting temperature is indicated.
from slightly different initial states and the temperature–pressure relation thus obtained is extrapolated to zero pressure to determine \( T_m \). In this work we used a simulation block with dimensions \( 49.6 \times 99.9 \times 47.6 \text{Å} \) containing 12240 atoms. The solid–liquid interface was parallel to the (1 1 1) plane and normal to the longest dimension of the simulation block. A linear fit to the pressure–interface was parallel to the (1 1 1) plane and normal to the longest dimension of the simulation block. A linear fit to the pressure–temperature points shown in Fig. 10 gives the melting temperature of \( 3301 \pm 0.5 \text{K} \). As an independent check, \( T_m \) was evaluated by NPT simulations using the same simulation block but annealed isothermally at several temperatures above and below the expected melting point. In such simulations, the solid–liquid interface migrates until one of the two phases disappears. The rate of migration was evaluated by the average energy change per unit time and extrapolated to zero rate (\( \text{Energy rate} \)). Several alternative functional forms of \( \phi_{\text{cut}}(r) \) and \( w_\text{cut}(r) \) were also tested, but it was found that Eqs. (10) and (11) offered the best accuracy of the fitting.

Since the pure Cu potential [22] is in the EAM format, the respective dipole and quadrupole interactions were set to zero. During the fitting of the mixed interactions, all potential functions were subject to invariant transformations [34,50,47] that did not affect properties of pure Cu and Ta but provided additional degrees of freedom for the optimization of mixed interactions. Such transformations involved three coefficients \( s_{\text{Ta}} \), \( s_\text{Cu} \), and \( g_\text{Ta} \), which were used as additional fitting parameters.

The potential functions (10) and (11) were fitted to first-principles formation energies of several imaginary Cu–Ta compounds with cubic structures (Table 3). Although none of these compounds exists on the Cu–Ta phase diagram, their role is to represent various structural and chemical environments that may occur during applications of the potential. As in the case of pure Ta, the fitting parameters were optimized by a combination of a genetic algorithm and simulated annealing. The optimized

### 5. ADP potential for the Cu–Ta system

#### 5.1. Potential format and fitting

For the binary Cu–Ta system, the mixed pair potential \( \Phi_{\text{CuTa}}(r) \) was represented by a Lenard–Jones potential with additional polynomial terms:

\[
\Phi_{\text{CuTa}}(r) = E_0 \left( \frac{a_1}{r} \right)^6 + \sum_{i=1}^{11} a_i \left( \frac{a_i}{r} \right)^{6-i} + a_0 \psi \left( \frac{r - r_c}{h} \right),
\]

(10)

where \( \psi(x) \) is the cutoff function defined by Eq. (6). The fitting parameters of \( \Phi_{\text{CuTa}}(r) \) are \( r_c \) and \( h \) and the \( a_i \)'s. The mixed quadrupole interaction function \( w_{\text{CuTa}}(r) \) was postulated in the form

\[
w_{\text{CuTa}}(r) = \psi \left( \frac{r - r_c}{h} \right) (q_1 e^{-q_2 r} + q_3),
\]

(11)

where \( q_1 \), \( q_2 \) and \( q_3 \) are three additional fitting parameters. The cutoff parameters \( r_c \) and \( h \) remain the same as in Eq. (10). Several alternative functional forms of \( \Phi_{\text{CuTa}}(r) \) and \( w_{\text{CuTa}}(r) \) were also tested, but it was found that Eqs. (10) and (11) offered the best accuracy of the fitting.

#### Table 3

<table>
<thead>
<tr>
<th>Phase Structure</th>
<th>( \text{Ab initio} )</th>
<th>ADP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuTa</td>
<td>B2*</td>
<td>0.1920; 0.2000; 0.1390</td>
</tr>
<tr>
<td></td>
<td>L1_2</td>
<td>0.1235; 0.2660; 0.0750</td>
</tr>
<tr>
<td></td>
<td>B2*</td>
<td>0.4841</td>
</tr>
<tr>
<td></td>
<td>B1*</td>
<td>0.7789; 0.7888</td>
</tr>
<tr>
<td></td>
<td>B3*</td>
<td>1.7421; 1.7550</td>
</tr>
<tr>
<td>Cu_2Ta</td>
<td>L1_2</td>
<td>0.3443; 0.3772; 0.3500</td>
</tr>
<tr>
<td></td>
<td>D0_0</td>
<td>0.1653; 0.1930</td>
</tr>
<tr>
<td></td>
<td>D0_1</td>
<td>0.1971</td>
</tr>
<tr>
<td></td>
<td>D0_2</td>
<td>0.1172; 0.1930</td>
</tr>
<tr>
<td></td>
<td>D0_3</td>
<td>0.1161; 0.1430</td>
</tr>
<tr>
<td></td>
<td>A15</td>
<td>0.3739</td>
</tr>
<tr>
<td>Ta_3Cu</td>
<td>L1_2</td>
<td>0.1490; 0.1585; 0.1265</td>
</tr>
<tr>
<td></td>
<td>D0_0</td>
<td>0.1822; 0.1895</td>
</tr>
<tr>
<td></td>
<td>D0_1</td>
<td>0.1393</td>
</tr>
<tr>
<td></td>
<td>D0_2</td>
<td>0.1596; 0.1660</td>
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<td></td>
<td>D0_3</td>
<td>0.1833; 0.1910</td>
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<tr>
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<td>Layer</td>
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<td>CuTaTa*</td>
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<tr>
<td></td>
<td>CuCuTa*</td>
<td>0.2190</td>
</tr>
<tr>
<td></td>
<td>CuTa*</td>
<td>0.1627; 0.0465</td>
</tr>
</tbody>
</table>

\* Ref. [51]
\[ \text{Ref. [52]} \]
\[ \text{Ref. [20]} \]
mixed-interaction functions $\Phi_{\text{CuTa}}(r)$ and $\Phi_{\text{CuTa}}(r)$ are shown in Fig. 12 together with the respective elemental functions. It should be emphasized that, due to the invariant transformations mentioned above, the Cu and Ta pair potentials look in this plot different from their original forms. In particular, the pair interaction $\Phi_{\text{CuTa}}(r)$ looks different from the curve plotted in Fig. 1. Nevertheless, when the binary potential developed here is applied to pure Cu or pure Ta, all properties of these metals are exactly the same as when using the original elemental potentials.

5.2. Properties of the Cu–Ta system

The imaginary compounds included in the potential fit had the relatively simple crystalline structures such as B1, B2, B3, L10, L11, L12 and D03. In addition, layered structures CuCuCuTaTa, CuCuTa and CuTaTa (see [20] for details) were also included. This set of compounds sample very diverse structures and different stoichiometries across the entire composition range between Cu and Ta.

Three sources of first-principles data for the structural energies were available for this work: the first-principles calculations by Hashibon et al. [20] and the quantum–mechanical databases developed by the groups of Curtarolo (AFLOW) [51] and Wolverton (OQMD: Open Quantum Materials Database) [52]. Certain discrepancies were found between the formation energies reported by the three sources, apparently arising from different choices of calculation parameters. To give an idea about the scatter of the data, we plot the predictions of Refs. [51,52] against each other for a set of simple structures selected for this work (Fig. 13(a)). The root-mean-square deviation between these datasets is 0.072 eV and Pearson’s correlation factor is 0.997. In view of these discrepancies, the first-principles energies used as input for fitting and testing of the potential were obtained by averaging the numbers coming from all sources available for any particular compound.

We were unable to achieve a perfect fit to all compounds chosen as targets. It was especially difficult to reproduce the formation energies of the layered structures without significant sacrifices in accuracy with respect to the simpler structures. We therefore chose the strategy of putting less weight on the layered structures and spreading the fitting errors more or less uniformly over the remaining compounds. Table 3 summarizes the results of fitting and testing. While for some compounds the agreement with first-principles data is good, for others the discrepancies can reach up to $\sim 0.1$ eV. Nevertheless, Fig. 13(b) demonstrates that the entire set of the ADP formation energies exhibits a significant correlation with first-principles data. The root-mean-square deviation between the ADP and first-principles energies is 0.089 eV and Pearson’s correlation factor is 0.978.

The zero-temperature energy of dilute solutions predicted by the ADP potential is 0.6771 eV for Cu in BCC Ta and 1.66471 eV for Ta in FCC Cu. Both energies are large enough to ensure that the mutual solid-state solubility between Cu and Ta be very small in agreement with the experimental phase diagram [12]. Calculation of the Cu–Ta phase diagram predicted by this potential is beyond the scope of this work. It is interesting to note, however, that the liquid Cu–Ta alloys exhibit a highly non-uniform structure consisting of nanometer-scale Ta clusters embedded in the Cu matrix. Similar thermodynamically stable nano-colloidal structures were found with the previous ADP potential [20] and were explained by a strong stabilizing effect of the Cu/Ta interface curvature [53]. The reproducibility of this unusual structure with two different potentials suggests that it is likely to be real and not an artifact of an interatomic potential.

6. Structural stability of Cu–Ta alloys

6.1. Methodology of simulations

A 3D polycrystalline Cu sample was constructed by the Voronoi tessellation method. Initially, 32 grain centers were selected as...
points of a regular FCC lattice but were subsequently randomized by adding random displacements. This ensured random sizes of the grains in the polycrystal. The Voronoi tessellation was performed using the free open-source program voro++ [54,55]. After the tessellation, the system was uniformly scaled in all three directions to the dimensions of $40 \times 40 \times 40$ nm with periodic boundary conditions in all three directions. Next, the polyhedra were filled with FCC Cu with crystallographic axes randomly orientated in space. Some overlap was initially allowed between the lattices of neighboring grains. Subsequently, the GB structures were optimized by identifying pairs of atoms separated by less than 0.6 of the equilibrium first-neighbor distance in FCC Cu and replacing them by a single atom. Further technical details of this procedure can be found in [56,57]. To further relax the GBs, the polycrystal was heated to the temperature of 300 K in 0.4 ns and annealed for another 0.4 ns by NPT MD simulations. These steps resulted in a 32-grain periodic polycrystalline sample containing about 5.4 million Cu atoms.

The initial grain size was estimated by $d_0 = \left(\frac{V}{N_g}\right)^{1/3} \approx 12.5$ nm, where $N_g = 32$ is the number of grains and $V$ is the system volume. During the subsequent grain growth simulations, the grain size $d$ was defined by $d = d_0 X_0/X$, where $X$ is the number of GB atoms and $X_0$ is the value of $X$ in the initial state. To determine $X$ for a given MD snapshot, the latter was quenched by static energy minimization and analyzed for bond angle distortions using the OVITO visualization tool [58]. The bond angle analysis identifies atoms with FCC and HCP environments, which correspond to the perfect FCC lattice and intrinsic stacking faults, respectively. The remaining atoms were attributed to GBs and their number was $X$. The implicit assumption of this calculation of $d$ is that the GB width remains constant, which may be a source of some error as the GB width may vary during the simulations.

Two types of Cu–Ta alloys were prepared. First, to model the non-equilibrium solid solution created by mechanical alloying, a set percentage of Ta atoms was introduced by random substitution of Cu atoms using a random numbers generator. As a result, the Ta atoms were randomly scattered over the system with the same density regardless of the GBs or grain interiors. Second, more equilibrium states of the alloy were prepared by semi-grand canonical Monte Carlo simulations [59] at zero pressure. In such simulations, the temperature $T$ and chemical potential difference $\Delta \mu$ between Ta and Cu are fixed while the distribution of Ta atoms over the system can vary to reach local thermodynamic equilibrium. The trial moves include displacements of randomly selected atoms by a random amount in a random direction with simultaneous random re-assignment of the chemical species of the chosen atom to either Ta or Cu. Simultaneously, the dimensions of the simulation block in all three directions are changed independently by random amounts with corresponding re-scaling of atomic coordinates. The trial move is accepted or rejected by a Metropolis algorithm. Further technical details of this method can be found in [60–62]. The simulation temperature was chosen to be 800 K at which no significant grain growth occurred during the Monte Carlo process, yet equilibrium could be reached by an affordable number of Monte Carlo steps. The chemical potential difference $\Delta \mu$ was adjusted to create several alloys with chemical compositions up to a few at.%Ta. It should be noted that these compositions are significantly higher than the Ta solid solubility limit in Cu. Thus, the alloys created by the Monte Carlo process are metastable and are intended to model the experimental alloys after a thermal treatment.

6.2. Simulation results

To model grain growth in pure Cu, the initial sample was heated to the temperature of 1200 K in 1.2 ns and annealed at this temper-
junctions as illustrated in Fig. 16(a). This microstructure is well consistent with experimental TEM observation that also show the preference of Ta clusters in nano-grained Cu samples [8].

To quantify the cluster size, the size distribution histograms were computed. To this end, all Cu atoms were removed from the relaxed MD snapshot and the remaining Ta atoms were processed by the cluster analysis algorithm implemented in the OVITO tool [58]. This analysis enabled us to construct the distribution function of the number of atoms in the clusters. This function is re-plotted in Fig. 17 as the normalized probability versus the cluster size $d_c$. The latter was defined by $d_c = (N_c V/N)^{1/3}$, where $N_c$ is the number of Ta atoms in the cluster and $N$ is the total number of atoms in the system. The plots are somewhat noisy because the statistics were obtained from only one snapshot (corresponding to the given simulation time) and the number of Ta atoms is relatively small due to the low Ta concentration. The first peak at $d_c < 0.5$ nm is caused by single Ta atoms and their small groups of 2–3 atoms. The second peak is caused by the nano-clusters, which have a typical size of about 0.7 nm. Note that the number of clusters (the peak height) tends to increase with the alloy concentration with only a small effect on the cluster size. This trend, and in fact the very existence of the peak, suggest that the clusters constitute a well-defined and well-reproducible structural feature of the alloy and are not caused by mere statistical fluctuations in the Ta distribution.

As demonstrated in Fig. 15(a), the addition of Ta in the form of clusters can drastically reduce the grain growth. While the addition of 0.1 at.%Ta has little effect, in the alloy with 0.3 at.%Ta the grain size increases only slightly and soon reaches a stagnation [63]. The alloys with $\geq 1$ at.%Ta exhibit no grain growth within the uncertainty of the calculations. The final structure of the 0.3 at.%Ta alloy after a 10 ns anneal is illustrated in Fig. 16(b). Most of the clusters remain at GBs, suggesting strong pinning. It is interesting to note, however, that a number of clusters can now be found inside larger grains that underwent some growth. Animations of the grain growth [63] confirm that such cluster initially formed at GBs, which were then able to break away from the clusters and leave them behind inside the grains. The strong pinning of GBs by Ta clusters is consistent with experimental studies of microstructure and thermal stability of nano-crystalline Cu–Ta alloys [8,9,7]. Such studies indicate that the precipitation of Ta clusters and larger particles at GBs drastically reduces the grain growth by the Zener pinning mechanism. The slight increase in the cluster size in the 4 at.%Ta alloy suggested by Fig. 17(b) can be explained by some coarsening due to Ta “short-circuit” diffusion along GBs. While the time scale limitation of MD prevents us from observing further growth of these cluster, their trend for coarsening is in agreement with the experimental observation of a large spectrum of cluster sizes, from a nano-meter size to a few tens of nanometers, with larger clusters located at GBs [8].

![Fig. 15](a) Average grain size versus time for several compositions of Ta in Cu–Ta alloys during isothermal anneals at 1200 K by NPT MD simulations. (a) Clustered Ta. (b) Randomly dispersed Ta.

![Fig. 16](a) Nanocrystalline Cu–0.3at.%Ta alloys (a) before and (b) after a 10 ns isothermal MD simulation at 1200 K. The GBs are revealed by bond angle analysis using OVITO [58]. The Ta atoms are shown in green and are larger than Cu atoms.
We now turn to alloys with randomly dispersed Ta atoms. In this case, the addition of Ta also reduces the grain growth (Fig. 15(b)), but the effect is not as strong as in the previous case. For example, while the addition of 1 at.%Ta in the form of clusters practically stops the grain growth (cf. Fig. 15(a)), the alloy with a random distribution of the same amount of Ta still shows some grain growth for the first 5 ns. In fact, a slight grain growth is even seen in the random 2 at.%Ta alloy [63].

Another interesting feature of Fig. 15(b) is that, for all compositions larger than 0.1 at.%Ta, the grain growth stops after about 5 ns, as it typically does also in the alloys with clusters. A plausible explanation of this effect is the formation of Ta clusters at the moving and stationary GBs during the anneal of random alloys. This is consistent with the images and animations [63] of the alloy structure. As an example, Fig. 18 shows a typical snapshot revealing initial stages of cluster formation in the random Cu-1at.%Ta alloy. The cluster formation is further confirmed by the cluster size distribution plotted in Fig. 19. As before, the sharp peak at small cluster sizes (< 0.3 nm) represents individual Ta atoms and their 2–3 atom clusters created by pure chance during the sample preparation. After the 10.8 ns anneal, a new peak begins to form reflecting the formation of larger clusters with the size of about 0.45 nm. If longer anneals could be afforded by our computation resources, we expect that the peak would grow in height and shift towards larger cluster sizes of about 0.8 nm. But already the observation of the early stages of peak formation combined with MD snapshots provide evidence for the clustering of the initially dispersed Ta atoms. These newly formed clusters eventually pin the GBs and stop the grain growth. This observation is consistent with experiments [8] and a possible mechanism for the formation of Ta clusters in GB locations during the heat treatment of mechanically alloyed Cu–Ta alloys [8].

7. Discussion and conclusions

We have developed an ADP potential for the Cu–Ta system by fitting to a large database of first-principles and experimental data and employing a combination of a genetic algorithm and simulated annealing for parameter optimization. We utilize an available EAM Cu potential [22] but construct a new ADP potential for Ta. We chose the ADP potential format [30,23,20,31,32] over the regular central force EAM for two reasons. First, the ADP format offers additional adjustable parameters that can be utilized for more accurate fitting to target properties. Second, and perhaps more important, the ADP format captures the directional component of chemical bonding and is more appropriate for BCC transition metals. For this reason, even if the accuracy of fitting to target properties is the same, an ADP potential can be expected to be more transferable to a wider set of properties of Ta and Ta alloys in comparison with regular EAM. Extensive tests show that the new potential accurately reproduces many properties of Ta and is transferable to severely deformed states and diverse atomic environments different from the equilibrium BCC lattice. The potential

Fig. 17. Ta cluster size distribution in Cu–Ta alloys before and after a 10 ns anneal at 1200 K. (a) Cu-0.1at.%Ta alloy. (b) Cu-4at.%Ta alloy. The initial clusters were created by a semi-grand canonical Monte Carlo simulation at 800 K.

Fig. 18. Snapshot of the Cu-2at.%Ta alloy after a 10.8 ns isothermal MD simulation at 1200 K. The initial state was created by purely random dispersion of Ta atoms. The GBs are revealed by bond angle analysis using OVITO [58]. The Ta atoms are shown in green and are larger than Cu atoms.

Fig. 19. Ta cluster size distribution in Cu-1at.%Ta alloy before and after a 10.8 ns anneal at 1200 K. The initial state was created by purely random dispersion of Ta atoms.
should be widely applicable to simulations of thermal and mechanical properties of Ta in the future. It is more accurate than most of the previously proposed Ta potentials and is comparable in accuracy with the recently developed EAM potential by Ravelo and co-workers [29]. In fact, the ADP potential shows some improvements over [29] with respect to surface energies, interstitial formation energies and the melting point. For example, the melting temperature predicted by the ADP potential is within a few degrees from the experimental value. Given that the ADP format is physically more appropriate for Ta, we believe that in the long run, the proposed potential will demonstrate a better reliability in a wide range of applications than could not be achieved within the standard EAM framework [21].

To obtain the binary Cu–Ta potential, the elemental Cu and Ta potentials have been crossed by fitting the mixed-interaction functions to first-principles energies for a set of imaginary intermetallic compounds that do not exist on the phase diagram but sample various atomic environments and chemical compositions.

The main application of the proposed Cu–Ta potential that motivated the present work is the problem of structural stability and strength of nano-crystalline Cu–Ta alloys. Detailed atomistic simulations of these properties are the subject on ongoing work and strength of nano-crystalline Cu–Ta alloys. Detailed atomistic calculations of the GB and interface free energies and heterogeneous nucleation hypothesis requires a special study involving calculations of the GB and interface free energies and the elastic strain energies associated with the cluster formation.

The present simulations also reproduce the drastic retardation effect of Ta on the grain growth kinetics known from experimental studies [8] as well as previous simulations [7]. The fact that nearly all Ta atoms located at GBs exist in the form of clusters is a strong indication that the retardation effect is due to the Zener pinning mechanism. It is most likely that in this class of alloys, other stabilization mechanisms, such as solute drag or reduction in the GB free energy by segregation, are less important. The rare GBs that were able to break away from the Ta clusters remained pure Cu boundaries and only stopped when encountered other clusters.

Finally, previous simulations [7] have revealed a significant increase in tensile strength caused by Ta alloying. While this conclusion is in agreement with experiment [8], the exact strengthening mechanism responsible for this effect remains elusive. As was mentioned in Section 1, the preservation of the small grain size alone cannot explain the strength in excess of the Hall–Petch relation [8]. Atomistic simulations of the deformation process may provide insights into the effect of the GB clusters on deformation mechanisms leading to the high strength of Cu–Ta alloys.

**Acknowledgments**

We are grateful to Dr. Ramon Ravelo for providing first-principles data for the gamma surfaces and tensile compression stresses from Ref. [29] in numerical format, which enabled direct comparison with the ADP predictions in Figs. 3 and 6. This work was supported by the U.S. Army Research Office under a contract number W911NF-15-1-0077.

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/10.1016/j.actamat.2015.08.052](http://dx.doi.org/10.1016/j.actamat.2015.08.052). These data include animations of Figures 14, 16 and 18 of this article.

**References**


