Atomic insights in crystallization of liquid Cu on single crystal Ta and amorphous Ta

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Abstract
The crystallization processes of liquid Cu on single crystal Ta and amorphous Ta under different undercoolings were investigated with molecular dynamics simulation. As the undercooling is not greater than 350 K, only heteronucleation process occurred in both cases. However, at a larger undercooling (400 K), the nucleation transformed from a heteronucleation mode to a mix-mode of heteronucleation and homonucleation in both cases. Interestingly, we found that the heteronucleation of Cu embryos, in the amorphous-Ta/liquid-Cu samples, was always triggered by the recrystallization of amorphous Ta; it means that crystal Ta possesses a higher nucleation potency than amorphous Ta. Further analysis indicated that the higher nucleation potency of single crystal Ta originates from its ability to induce liquid Cu atoms ordering. Liquid Cu took a longer time, on average, to nucleate on amorphous Ta than on crystal Ta at different temperatures. In addition, microstructure analysis indicated that the crystallized region contained both stacking faults and twin crystals.

1. Introduction
Heteronucleation is a ubiquitous phenomenon, which has attracted extensive interest because of its importance in fundamental research and materials engineering [1–7]. In this complex process, the nucleation mechanism may vary dramatically upon change of conditions, such as the nucleant, impurity, undercooling and so on [2, 7]. In practical perspectives, the understanding of heteronucleation mechanism in different conditions would inspire the control of materials properties towards diverse applications [8]. The heteronucleation occurring on crystals has been extensively investigated by both experiments and computational simulations, and the findings have extended our understanding on this subject. For instance, the heteronucleation mechanism of Al on different nucleants was frequently studied. Wang et al [5, 6] disclosed that the nucleants terminated with different atom planes exhibited different potency. Palafox-Hernandez et al [4] observed the orientation dependence of heteronucleation in Cu-Pb system. All these findings indicate that heteronucleation strongly depends on the surface structure of the nucleants, and the lattice misfit between the nucleant and the nucleated crystal was treated as the main factor to evaluate the potency of nucleant [1]; in general, the smaller the misfit, the higher the nucleation potency. Zhang et al [1] found that adding Ti solutes in Al melt could facilitate Al to nucleate on TiB2 by relieving the misfit between nucleant TiB2 and Al. Similar solute effect was also observed in Wang’s experiment about heteronucleation of Al-Cu alloy [9].

Amorphous and crystalline materials have distinct microstructure characteristics; therefore, the heteronucleation occurring on these two types of materials should have different mechanisms. Moreover, many amorphous/crystalline composites exhibit excellent properties [10–12], understanding the heteronucleation mechanism on amorphous materials makes it possible to control the structure and properties of the composites. Thus, whether from the view of developing basic theory or solving engineering problems, it is necessary to take a comparative study of the heteronucleation on crystalline and amorphous substrates. Although some researches paid attention to the heteronucleation on amorphous substrates [13–15], few work focused on the differences of heteronucleation on crystalline and amorphous materials, especially at an atomic scale. Akazawa [2] studied the deposition of ZnO on glass and sapphire c-planes, the results suggested that the crystallinity of ZnO near the
glass/ZnO interface was lower than that near the sapphire/ZnO interface. Using molecular dynamics simulation, An et al. [16] found that spraying high temperature liquid Cu nanodroplets on amorphous substrate (Cu₄6Zr₅₄) obtained amorphous Cu, while spraying the same nanodroplets on crystalline substrate (Cu) obtained crystal Cu. Such results indeed indicate that crystalline and amorphous substrates possess different nucleation potency. However, it is also noteworthy that the components of the crystalline and amorphous substrates used in the aforementioned cases are different, so it is impossible to independently evaluate the roles of structure and component of the substrates played in these experiments. Decoupling these two factors and revealing how the substrate’s structure variation (from a crystalline state to an amorphous state) influencing the heteronucleation on it is meaningful. In order to concentrate on the structure effect, the component effect was excluded by choosing an elementary substance which can form crystalline and amorphous structures at the same time.

In this work, the Ta–Cu system was selected as the ideal target because Ta can form amorphous and crystalline structures; in addition, Ta and Cu have larger difference in melting point [17]. The crystallization processes of liquid Cu on single crystal Ta and amorphous Ta were investigated with molecular dynamics simulation, and we also studied the undercooling effect on the crystallization process. It was found that amorphous Ta possesses a lower nucleation potency than single crystal Ta, and the nucleation of Cu embryos on amorphous Ta was always triggered by the recrystallization of amorphous Ta. These findings deepen our understanding about nucleation on amorphous substrates.

2. Simulation details and methods

All the simulations were implemented with the large-scale atomic/molecular massively parallel simulator (LAMMPS) [18] combined with the potential proposed by Pun et al. [19] and Mishin et al. [20]. The potential is a hybrid of embedded-atom method potential and angular-dependent potential, in which the Cu–Cu interaction is described by embedded-atom method potential and the Ta–Ta and Cu–Ta interactions are described by angular-dependent potential. The potential can well reproduce many properties of Ta, Cu and Cu-Ta alloy, the calculated melting points of Ta and Cu are about 3301 K and 1315 K, respectively, which agree well with the experimental values of 3293 K and 1353 K. Three steps were carried out to construct the Ta(Cu1)–Cu crystalline-liquid interface samples (hereafter we call them C-L samples). First, a body-centered cubic (bcc) Ta with the size of 30aTa × 30aTa × 20aTa (aTa is the lattice constant of Ta at 0 K) was relaxed with NPT ensemble (constant pressure and constant temperature) for 0.5 ns at 915 K, 965 K and 1015 K, respectively. Then three fcc Cu samples with the size of 27aCu × 27aCu × 27aCu were melted at 1800 K with NPT ensemble for 0.4 ns, in which the samples relaxed freely along the z axis while the lengths along the other two dimensions were fixed to match with the size of the Ta samples obtained in step one at 915 K, 965 K and 1015 K, respectively. It is necessary to state that the lattice constant of Cu aCu was slightly adjusted to achieve a good size match with the Ta samples in the xy plane. After melting, the liquid Cu samples were cooled to the temperatures as the Ta blocks were set, respectively, at the same speed of 1.67 × 10¹² K s⁻¹. At last, the C-L samples were assembled by conjoining the crystal Ta and liquid Cu samples along the z axis. To weaken the strong interaction at the interface caused by atom superposition, a 2.7 Å gap was inserted between the Ta and Cu blocks. An analogical procedure was adopted to construct the Ta–Cu amorphous-liquid interface samples (hereafter we call them A-L samples), while the first step was replaced by melting Ta blocks at 4500 K with NPT ensemble for 0.5 ns and then quenching them to 915 K, 965 K and 1015 K, respectively, at a speed of 1.76 × 10¹¹ K s⁻¹ to obtain amorphous TAs. The assembled samples were relaxed 1.0 ns with NPT ensemble to investigate the crystallization process of liquid Cu. For avoiding the randomness of the result, five independent samples (hereafter referred as sample 1–5) were constructed for each sample type at each temperature. Periodic boundary condition was adopted for all simulations and the timestep was set as 1.0 fs, temperature and pressure were controlled with the Nose-Hoover thermostat [21, 22] and Parrinello barostat [23], respectively.

3. Results and discussions

Figure 1(a) shows the fine-scale density profiles of Ta and Cu atoms along the interface normal of the C-L sample 1 at 965 K after 0.02 ns relaxation, the narrow transition region indicates that the interdiffusion between these two kinds of atoms is very slow. In order to clearly exhibit the microstructure evolution process of the samples, a series of intermediate configurations were captured and analyzed with the adaptive common neighbor analysis (ACNA) method [24], which can accurately identify the atoms in different structures. In the ACNA method, the atoms in a sample can be identified as different types (bcc, fcc, hcp or other types) according to the local structure it formed with its neighbors (two atoms are said to be neighbors, or bonded, if they are within a specified cutoff distance rcut). And the local structure around a specific atom is characterized by a set of indexes N(n1 n2 n3). n1
represents the number of common neighbors shared by the target atom and one of its neighbors, \( n_2 \) is the number of bonds formed among the \( n_1 \) common neighbors, \( n_3 \) is the number of bonds in the longest atom chain formed among the \( n_1 \) common neighbors, and \( N \) is the number of configurations described by \((n_1 \ n_2 \ n_3)\). Analysis indicates that the atoms in bcc, fcc and hcp phases form particular local structures with their 14 (for bcc phase) or 12 (for fcc and hcp phases) nearest neighbors, and the corresponding local structures can be uniquely characterized by a set of indexes listed in Table 1. Thus, the structure type of each atom can be determined according to its local structure indexes. In the ACNA method, for identifying the structure types of atoms in multiphase materials, the cutoff distance \( r_{\text{cut}} \) is varied to include different neighbors when calculating the structure indexes of an atom. The time-dependent ACNA results of the C-L sample 1 at 965 K are presented in Figure 2, in which only the atoms in fcc, hcp or bcc structures are picked out to analyze the nucleation and growth process of crystal Cu. A typical heteronucleation and growth process can be observed, two stable crown-like Cu embryos preferentially formed at the interfaces after about 0.12 ns relaxation and then grew rapidly as time increased, while during the simulation no embryo nucleated in the bulk phase. It is very similar to the heteronucleation process of liquid Pb on Cu(100) surface [4]. Besides fcc atoms, the crystallized region also contains a large number of hcp atoms, which is attributed to the close cohesive energy of these two phases [25]. The fcc and hcp atoms form an alternative layer-structure. In the other four samples, the nucleation-growth process shows similar characteristics as those described above, which indicate the results are universal and do not depend on the initial configuration of the samples.

Compared with the nucleation-growth process in the C-L samples, some similarities and differences emerged in the evolution process of the A-L samples. Take the A-L sample 1 as an example. The narrow transition region in the fine-scale density profiles (shown in Figure 1(b)) also implies a very slow interdiffusion process between Ta and Cu atoms, despite the Ta block being in a metastable amorphous state, which is consistent well with the experiment result [26]. In addition, the time-dependent ACNA results (shown in Figure 3) also present evident characteristics of heteronucleation as those observed in the C-L samples. More specifically, one Cu embryo, composed of fcc and hcp atoms, preferentially nucleated at the interface and then grew rapidly; the hcp atoms also formed lamellas and inserted in the fcc phase. According to the results of stacking analysis (shown in Figure 4), it was found that the single and double hcp layers in both the C-L and A-L samples are twin boundaries and stacking faults. More attention should be paid to the differences, which reflect

![Figure 1](image_url). Fine-scale density profiles of Ta and Cu atoms along the interface normal of (a) the C-L sample 1 and (b) the A-L sample 1 at 965 K after 0.02 ns relaxation.

|                  | bcc | fcc | hcp |
|------------------|-----|-----|-----|
| Local structure index 1 | 8(6 6 6) | 12(4 2 1) | 6(4 2 1) |
| Local structure index 2 | 6(4 4 4) | 6(4 2 2) |
Figure 2. Time-dependent ACNA results of the C-L sample1 at 965 K.

Figure 3. Time-dependent ACNA results of the A-L sample1 at 965 K.
the influence on the nucleation-growth process when the nucleant changes from a crystalline state to an amorphous state. Firstly, the amorphous Ta recrystallized gradually during the simulation because of the relative higher temperature. More interestingly, it took a longer time (about 0.58 ns) for the Cu embryo to nucleate, and the Cu embryo rooted on a small recrystallized region of the amorphous Ta despite the fact that the amorphous region occupying the vast majority of the interface area. Based on these results, we speculated that the Cu embryo’s nucleation may correlate with the recrystallization of the amorphous Ta. In order to demonstrate the speculation, the other four independent samples were carefully analyzed; as expected, the Cu embryos always rooted on the recrystallized regions and never on the amorphous region (not shown here). It means that amorphous Ta is not benefit for the nucleation of Cu embryos. The low nucleation potency of some other amorphous materials was also reported in previous studies [2, 16]. To further verify our speculation, more targeted simulations were carried out, in which the Ta atoms were fixed to inhibit the recrystallization of the amorphous Ta. If the Cu embryos’ nucleation is indeed related with the recrystallization of the amorphous Ta, it would be impossible to observe the formation of the Cu embryos during these simulations when the undercooling is not enough to trigger homonucleation process. As expected, the amorphous Ta did not recrystallize and no Cu embryo formed in these simulations within a period of 2.0 ns (the ACNA result of a typical sample is shown in figure 5), which, again, strongly confirms our speculation. It is now clear that amorphous Ta possesses a lower nucleation potency than its crystalline counterpart, and the heteronucleation of the Cu embryos is closely connected with the recrystallization of amorphous Ta.

Undercooling is an important factor that influences nucleation, larger undercooling means larger driving force, in that case it is possible for Cu embryos to nucleate on amorphous Ta. In order to investigate the undercooling effect, simulations were also carried out at 915 K and 1015 K for both the C-L and A-L samples. At these two temperatures, the nucleation-growth process also presented the main characteristics as those observed in the corresponding samples at 965 K. Besides such characteristics, remarkable undercooling effect appeared as well; and a typical microstructure evolution process of the C-L samples at 915 K is illustrated in figure 6. Both the nucleation site and nucleation time were chose to analyze the undercooling effect. According to the nucleation site, the samples were classified into three types including ‘interface’, ‘bulk’ and ‘interface-bulk’, in which the Cu embryos nucleated at the interface, in the bulk of liquid Cu or both at the interface and in the bulk of liquid Cu, respectively. If no embryo nucleated in a sample during the simulation, we labeled it with ‘none’. For simplicity, the time interval from the start of simulation to the point when the total number of fcc and hcp Cu atoms began increasing explosively was roughly defined as the nucleation time. The calculated results of the sample numbers with different nucleation site and the average nucleation time are illustrated in figure 7. As shown in figure 7(a), at 965 K, the liquid Cu crystallized in all the C-L and A-L samples and the embryos all nucleated at the interface. It is worth emphasizing that all the embryos formed in the A-L samples rooted on the recrystallized region of amorphous Ta. As the undercooling increased (at 915 K), Cu embryos formed not only at the interface but also...
Figure 5. Time-dependent ACNA results of the A-L sample1 at 965 K (in which the Ta atoms were fixed during the simulation).

Figure 6. Time-dependent ACNA results of the C-L sample1 at 915 K.
in the bulk phase (see figures 6 and 7(a)), which means this undercooling is enough to induce homonucleation and the nucleation gradually transformed from a heteronucleation mode to a mix-mode of heteronucleation and homonucleation. Unfortunately, in the A-L samples, there is still no Cu embryo nucleating on the amorphous region of Ta even with such a large undercooling. Obviously, this result implies that the homonucleation barrier is smaller than the heteronucleation barrier that should be overcome when nucleating on the amorphous Ta. The Cu embryos nucleated much faster on average than those formed at 965 K in the corresponding samples (shown in figure 7(b)), suggesting a larger driving force in this condition. On the contrary, at a smaller undercooling (at 1015 K) homonucleation was not triggered; and the heteronucleation process averagely took a longer time, even more than half of the C-L samples were still in an uncrystallized state after 3.0 ns relaxation (see figure 7(a)). In this condition, only the crystallized samples were counted when calculated the average nucleation time. In addition, we found that the embryos in the C-L samples nucleated faster on average than those formed in the A-L samples at a certain temperature, which agree well with the fact that the heteronucleation occurring in the A-L samples was triggered by the recrystallization of the amorphous Ta, and recrystallization needs extra time.

Why the heteronucleation of Cu embryos are always triggered by the recrystallization of amorphous Ta in the A-L samples? From an atomic view, nucleation means that a cluster of disordered atoms rearrange into an ordered state. A number of computer simulations and experiments found that crystalline materials can induce ordering in liquid [27–30], and we think that this phenomenon should be caused by the periodic distributed potential wells near the interface produced by the crystalline materials. Obviously, the ordering of liquid atoms is benefit for its nucleation, which was validated with molecular dynamics simulation in the Cu-Pb system [4]. From the fine-scale density profiles (see figure 1(a)), we can detect three distinct density peaks of Cu atoms near the Ta(001)/Cu crystalline-liquid interface, which is an evident signal of ordering of liquid Cu atoms. Due to the disordered characteristic, amorphous Ta cannot generate periodic distributed potential wells near the interface; therefore it loses the ability to induce liquid Cu atoms ordering (no distinct Cu density peaks near the Ta/Cu amorphous-liquid interface, see figure 1(b)), making liquid Cu nucleating on it more difficult than on single crystal Ta. When the amorphous Ta recrystallized near the interface, the recrystallized regions regained the ability to drive liquid Cu atoms ordering, that is why the Cu embryos always rooted on those regions.
4. Conclusions

Using molecular dynamics simulation, the crystallization processes of liquid Cu on single crystal Ta and amorphous Ta were studied. Due to the immiscible nature, the interface transition region is very narrow even in the Ta/Cu amorphous-liquid samples. The ACNA results vividly exhibited the microstructure evolution during the crystallization processes. Typical heteronucleation process, namely the Cu embryos preferentially forming at the amorphous Ta, which indirectly reflects the higher nucleation potency of crystal Ta than its amorphous counterpart. Moreover, it was found that the higher nucleation potency of crystal Ta is closely correlated with its ability to induce liquid Cu atoms ordering. As the undercooling increased, the nucleation transformed from a heteronucleation mode to a mix-mode of heteronucleation and homonucleation in both the C-L and A-L samples. For heteronucleation, liquid Cu took a longer time, on average, to nucleate on amorphous Ta than on single crystal Ta at all temperatures. Detailed microstructure analysis indicated that the hcp atom layers embedded in the fcc phase mainly are stacking faults or twin boundaries. This work enriches our fundamental understanding about heteronucleation on amorphous substrate.

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