Molecular dynamics simulation of heterogeneous nucleation via grain refiner inoculated in aluminium melt

Takuya Fujinaga and Yasushi Shibuta
Department of Materials Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
E-mail: fujinaga@mse.mm.t.u-tokyo.ac.jp

Abstract. Since it is not straightforward to directly observe nucleation at the initial stage of solidification in experiments, investigation from computational approach is strongly desired. In this study, influence of grain refiner in heterogeneous nucleation of undercooled Al melt is investigated by molecular dynamics calculations. Particularly, we focus temperature, size of the refiner, and anisotropy in surface orientation of the grain refiner. It is confirmed that the growth rate of FCC Al at the (0001) plane is much larger than that at the other surfaces at all temperatures calculated in this study. Moreover, epitaxial growth of HCP Al appears on the surface of (1010) and (1120) planes at large undercooling temperature.

1. Introduction
Since most metallic materials are formed through solidification from undercooled melt, it is indispensable to control nucleation at the initial stage of solidification [1]. However, it is not straightforward to directly observe nucleation process in experiments and therefore computational researches have contributed the understanding a fundamental aspect of nucleation [2,3]. Especially, molecular dynamics (MD) simulations have shed light on atomistic details of nucleation [2-4]. At present, a billion-atom MD simulation is achieved to investigate homogeneous nucleation from undercooled melt of pure metals owing to recent advance in high-performance computing [4]. On the other hand, heterogeneous nucleation usually occurs in actual production process. Moreover, heterogeneous nucleation is often promoted by inoculating grain-refiners in the melt to produce fine microstructure [5,6]. Although most of the current MD studies on nucleation focus on homogeneous nucleation mainly due to the limitation of interatomic potentials, recent advance in development of interatomic potentials of multi-component systems [7] expands the availability of MD simulations on metallurgical processes such as phase transformation in alloy system and heterogeneous nucleation from hetero-walls or grain refiners. In this study, heterogeneous nucleation of Al melt from a surface of grain refiner is investigated by an MD simulation, which is not straightforward to be observed by experiments. Here, Ti and Ti₃Al are employed as grain refiners since Ti-based compounds are often used as grain refiners [6].

2. Methodology
In this study, MD simulations are performed using LAMMPS (Large-scale Atomic/Molecular Massive Parallel Simulator) [8]. An EAM (embedded atom method) potentials fitted by Zope and Mishin [9] is employed as an interatomic potential of Al-Ti interaction. Parameter files for the EAM potentials from the database of NIST-IPR project [7] are utilized for simulations by the LAMMPS. The velocity-
Verlet method is used to integrate the classical equation of motion with a time step of 1.0 fs. The Nose-Hoover thermostat and barostat [10,11] are employed to control temperature and pressure. OVITO (Open visualization tool) [12] is used for visualization of atomic configuration and post-analyses of calculation results such as adaptive common neighbor Analysis (a-CNA) [13].

Figure 1 shows an initial configuration of the calculation system, which is prepared as follows. Firstly, a liquid Al is obtained by annealing a face-centered cubic (FCC)-Al crystal consisting of 120 × 120 × 120 unit cells (6,912,000 atoms) at 2000 K for 10 ps with the number of atoms, volume and temperature (NVT)-constant ensemble. Separately, Ti or Ti$_3$Al cubic particles with various sizes (approximately 5, 8, 10 and 15 nm on a side) are cut out from a hexagonal column of hexagonal-close-packed (HCP)-Ti or D0$_19$-Ti$_3$Al and annealed at 500 K during 10 ps. Here, cubic particles are employed to investigate the effect of surface orientation on nucleation behavior. Then, one cubic particle is inserted in the center of Al melt, while omitting liquid atoms located within 2.5 Å from Ti atoms and energy minimization is performed for the combined structure to avoid unexpected proximity between liquid Al and solid Ti at the interface. Prepared structures are relaxed at 700 and 500 K for 300 ps with the number of atoms, pressure and temperature (NPT)-constant ensemble and growth behavior of solid Al on the surface of the cubic particle is investigated. Moreover, a system filled out with Al melt only (i.e. no grain refiner) is annealed at 700 and 500 K for comparison. Prior to main MD simulation, melting point of pure Al of this EAM potential is estimated by the convergence temperature technique [14, 15] and it is estimated to 870 K. Therefore, annealing temperatures, 700 and 500 K correspond to the undercooling temperature, 170 and 370 K, respectively. Note that the undercooling temperature in this study is larger than that of typical experimental conditions to accelerate nucleation event within the time scale of MD simulation.

3. Results and discussion

Figure 2 shows snapshots of atomic configuration during heterogeneous nucleation at surfaces of Ti and Ti$_3$Al particles of ca. 8 nm at 700 and 500 K. In general, FCC phase of Al is nucleated from the (0001) plane of both Ti and Ti$_3$Al particles and it grows hemispherically at both temperatures. In the case of 700 K, there is no nucleation at other planes but only a few layers of HCP Al appear on the surface of these planes. Then, area of FCC phase of Al nucleated on the (0001) plane comes around the other planes and finally, almost all surfaces of the particle are covered by FCC phase of Al. On the other hand, HCP phase of Al grows on (1010) and (1120) planes until it is trapped by FCC phase, which comes in front proactively in the case of 500 K. Then, the area of HCP phase gradually changes into FCC
phase. It is considered that purple lines in FCC phase represent stacking faults rather than residual HCP phase. Regarding species of the grain refiner, there is no significant difference in the growth behavior of FCC phase of Al between Ti and Ti$_3$Al particles within the range of simulation time. However, growth velocity of FCC phase of Al on Ti$_3$Al particle is slightly faster than that on Ti particle. Figure 3 shows

Figure 2. Snapshots of atomic configuration during heterogeneous nucleation at the surface of Ti and Ti$_3$Al particles of 8 nm at (a) 700 and (b) 500 K.

Figure 3. Snapshots of atomic configuration after 300 ps simulation with various sizes of particles: (a) Ti and (b) Ti$_3$Al particles.
snapshots of atomic configuration after 300 ps simulation with various sizes of particles. At a glance, there is no significant difference in growth behavior with respect to particle size within the range of calculation. As shown in Figure 2, FCC phase of Al is nucleated from the HCP(0001) plane, which is equivalent to the FCC(111) plane. Furthermore, HCP phase grown from (10\bar{1}0) and (11\bar{2}0) planes changes into FCC phase when the size of the Ti particle is 8 nm or less, at 500 K. It is confirmed that HCP structure appears just after the nucleation but it could not be retained.

Figure 4 shows a schematic image of generation process of Al nuclei on the Ti surface. On the (0001) plane, Al atoms come at a B-layer position of FCC Al on the HCP Ti plane first. Once B-layer positions are filled, Al atoms come at a C-layer position next, which forms a FCC structure. In other aspects, Al crystal is generated in accordance with the crystal structure of Ti or Ti₃Al particle, which is regarded as epitaxial growth. In the same manner, epitaxial growth occurs on (10\bar{1}0) and (11\bar{2}0) planes. That is, the HCP layer appears as illustrated in Figure 4. However, the growth of HCP layer stops after only a few layers appears at 700 K since HCP phase is not the most stable for Al. However, HCP phase keeps growing until it is trapped by the FCC phase at 500 K (i.e., a large undercooling temperature) as confirmed in Figures 2 and 3. To discuss it from energetic viewpoint, we calculate cohesive energies of FCC-Al, HCP-Al with a same bond length with FCC-Al (HCP1 in Table 1), and HCP-Al with a lattice constant of Ti (HCP2 in Table 1) using the present EAM potential. Since the cohesive energy of FCC-Al takes the minimum value (i.e. the most stable), it is reasonable that FCC-Al nucleates preferentially on the Ti and Ti₃Al surface. However, epitaxial growth of HCP-Al is partially observed on (10\bar{1}0) and (11\bar{2}0) surfaces since the energy difference between FCC-Al and HPC-Al is relatively small.

Table 1. Cohesive energy of Al crystal for FCC and HPC structures by present EAM potential.

| Crystal structure | FCC  | HCP1  | HCP2  |
|-------------------|------|-------|-------|
| Lattice constant [Å] | 4.05 | 2.83  | 2.95  |
| Cohesive energy [eV/atoms] | -3.35998 | -3.31983 | -3.31558 |
In order to compare a growth rate of solidified Al structures on each plane of Ti and Ti$_3$Al particles, a kinetic coefficient of Al is estimated from temperature dependency of solid-liquid interfacial velocity of Al as follows. The propagation velocity of solid-liquid interface of Al is measured on the system connecting Ti or Ti$_3$Al solid with a target orientation and Al liquid. This biphasic system is relaxed at 400, 500, 600, 700, 800 and 900 K at 300 ps. Then, the slope of the interfacial velocity as a function of temperature is defined as a kinetic coefficient. Technical details of this method is shown in elsewhere [16]. Note that the interfacial velocity of HCP-liquid interface is measured for (10\overline{1}0) and (11\overline{2}0) planes whereas that of FCC-liquid interface is measured for (0001) plane. Figure 5 shows kinetic coefficients of solid-liquid interface of Al solidified from Ti and Ti$_3$Al surfaces with various orientations. The kinetic coefficient for the (0001) plane is much larger than those at the other planes, which is consistent with our MD results as shown in Figures 2 and 3. Also, kinetic coefficients for Ti$_3$Al surfaces become larger than those for Ti surface. It is also consistent with our MD results that Al growth from Ti$_3$Al particles is faster than that from Ti particles.

4. Conclusions
In this study, MD simulations are performed to investigate the influence of grain refiner in heterogeneous nucleation of undercooled Al melt. It is confirmed from simulation results that the growth rate of FCC Al at the (0001) plane is much larger than that at the other surfaces at all temperatures calculated in this study. Although only a few layers of HCP Al appear on the surface of (10\overline{1}0) and (11\overline{2}0) planes at 700 K, epitaxial growth of HCP Al appears at 500 K. For all orientations, growth rate of Al from Ti$_3$Al particles is faster than that from Ti particles, which is also confirmed from the kinetic coefficient.

In summary, it is significant in this study to shed light on the heterogeneous nucleation at grain refiners inoculated in Al melt since it is not straightforward to observe it at atomistic scale from experimental measurement. The relationship between undercooling temperature (especially in the range of small undercooling temperature) and particle size, which is a key factor of a free growth model [6,17], will be investigated in the next step.

Acknowledgements
This work was supported by Grant-in-Aid for Scientific Research (B) [No.16H04490] from Japan Society for the Promotion of Science (JSPS), Japan.
References

[1] Dantzig J A and Rappaz M, Solidification 2009 (Lausanne: EPFL Press) pp. 249-285.
[2] Shibuta Y, Ohno M and T. Takaki 2015 JOM 67 1793.
[3] Shibuta Y, Ohno M and T. Takaki 2018 Adv. Theo. Sim. 1 1800065.
[4] Shibuta Y, Sakane S, Miyoshi E, Okita S, Takaki T and Ohno M 2017 Nat. Commun. 8 10.
[5] Hamilton R W, Forster M F, Dashwood R J and Lee P D 2002 Scr. Mater. 46 25.
[6] Greer A L, Cooper P S, Meredith M W, Schneider W, Schumacher P, Spittle J A and Tronche A 2003 Adv. Eng. Mater. 5 81.
[7] Becker C A, Tavazza F, Trautt Z T and Buarque de Macedo R A 2013 Curr. Opin. Solid State Mater. Sci. 17 277, http://www.ctcms.nist.gov/potentials.
[8] Plimpton S J 1995 J. Comput. Phys. 117 1, http://lammps.sandia.gov.
[9] Zope R R and Mishin Y 2003 Phys. Rev. B 68 024102.
[10] Nose S 1984 J. Chem. Phys. 81 511.
[11] Hoover W G 1985 Phys. Rev. A 31 1695.
[12] Stukowski A. 2010 Model. Simul. Mater. Sci. Eng. 18 015012.
[13] Stukowski A. 2012 Model. Simul. Mater. Sci. Eng. 20 045021.
[14] Shibuta Y and Suzuki T 2007 Chem. Phys. Lett. 445 265.
[15] Shibuta Y, Takamoto S and Suzuki T 2008 ISIJ Int. 48 1582.
[16] Watanabe Y, Shibuta Y and Suzuki T 2010 ISIJ Int. 50 1158.
[17] Greer A L and Quested T E 2006 Philo. Mag. 86 3665.