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Effect of samarium doping on the nucleation of fcc-aluminum in undercooled liquids

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ABSTRACT

The effect of Sm doping on the fcc-Al nucleation was investigated in Al-Sm liquids with low Sm concentrations (x_{Sm}) with molecular dynamics simulations. The nucleation in the moderately undercooled liquid is achieved by the recently developed persistent-embryo method. Systematically computing the nucleation rate with different x_{Sm} (x_{Sm} = 0%, 1%, 2%, 3%, 5%) at 700 K, we found Sm dopant reduces the nucleation rate by up to 25 orders of magnitudes with only 5% doping concentration. This effect is mostly associated with the increase in the free energy barrier with minor contribution from suppression of the attachment to the nucleus caused by Sm doping.

Al-based alloys are widely used as materials for engineering and manufacturing due to their low density and high specific strength [1]. In addition, there is extensive interest [2–14] in glass forming alloys because of their superior mechanical properties. Among the class of glass-forming binary alloys, Al-rare-earth (Al-RE) amorphous alloys form a special subclass [15] because the glass formation range in Al-RE binary alloys lies on the solute-rich side of the eutectic point which violates the general rule that the binary metallic glass forms near the eutectic region [13, 16, 17]. In this paper, we focus on the Al—Sm system [11], a typical example of the glass forming Al-RE alloys [16], to study the effects of Sm doping on the nucleation of the face-centered cubic (fcc) Al crystals. Our study aims to elucidate the mechanism by which minor doping of RE elements can dramatically change the phase selection process by avoiding nucleation of fcc Al in the undercooled liquid [18].

Molecular dynamics (MD) simulation is an excellent tool that provides detailed information for phase transformations on the atomic level [19]. Recent MD simulations have revealed the nucleation kinetics in AlSm metallic glass [20] and the detailed growth kinetics of the devitrified AlSm crystal phases [21, 22]. It was found that in the AlSm metallic glass, the Sm solute can retard Al nucleation by increasing the kinetic barrier to reduce the nucleus attachment rate [20]. Although the kinetic barrier can be the dominant factor controlling the nucleation in the glass state [20], it remains unclear how the Sm solutes affect the Al nucleation in a moderately undercooled liquid. On the other hand, due to the limitation of the simulation time, conventional MD simulations cannot access the nucleation event in the timescale which corresponds to the most common experimental conditions to measure the nucleation rate [23, 24]. Here, we employ the recently developed persistent-embryo method (PEM) [25] to allow efficient sampling of rare Al nucleation events in the undercooled liquid. With the PEM, we are able to observe the Al nucleation without any biasing of the system when the critical nucleus forms which allows us to obtain accurate quantitative estimates of the critical nucleus size as a function of Sm doping. Within Classical Nucleation Theory (CNT), the simulation results can be used to compute the nucleation rate as a function of the Sm doping concentrations. Our results yield accurate quantitative estimates of contributions from thermodynamics versus kinetics effects of Sm addition.

According to the CNT [26], a homogeneous nucleation involves a formation of the critical nucleus in the undercooled liquid. The formation of such a nucleus is governed by two factors: one is the thermodynamic driving force towards the lower-free-energy bulk crystal. This term is negative and proportional to the nucleus size. The other is the energy penalty for creating an interface between the nucleus and the liquid. This term is positive and proportional to the area of the interface. Therefore, the excess free energy to form a nucleus with N atoms is.

$$\Delta G = N\Delta\mu + A\gamma \quad (1)$$

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where $\Delta\mu$ (<0) is the chemical potential difference between the bulk solid and liquid, γ is the solid-liquid interfacial free energy, and A is the interface area which can be evaluated as $A = sN^{2/3}$ with s being a shape factor. The competition between the bulk and interface terms leads to a nucleation barrier ΔG^* when the nucleus reaches the critical size N^*. CNT assumes the spherical shape for the nucleus to relate ΔG^* with γ and $\Delta\mu$. We lift this assumption by introducing the shape factor s, assuming that the shape of the sub-critical nucleus does not change during growth. Mathematically, the interfacial free energy density γ and the shape factor s, which are both difficult to compute, can be replaced by the critical nucleus size N^* at the critical point [25] in the expression of the free energy barrier ΔG^*, resulting in.

$$\Delta G^* = \frac{1}{2}|\Delta\mu|N^* \tag{2}$$

The crystal nucleation rate is the product of the probability to form the critical nucleus given by $\exp(-\Delta G^*/k_BT)$ and the kinetic prefactor. Following Auer and Frenkel [27], the expression of the nucleation rate can be written as:

$$J = \rho_L f^+ \sqrt{\frac{|\Delta\mu|}{6\pi k_B T N^*}}\ \exp\left(-\frac{|\Delta\mu|N^*}{2k_BT}\right) \tag{3}$$

where f^+ is the rate of single atom attachment to the critical nucleus and ρ_L is the liquid density. Four factors, ρ_L, N^*, $\Delta\mu$, and f^+, are needed to compute the nucleation rate at a given temperature T. The liquid density ρ_L can be obtained from the *NPT* simulation. The critical size N^* and the attachment rate f^+ can be obtained from molecular dynamical simulations using the persistent-embryo method. The chemical potential difference $\Delta\mu$ is calculated separately using thermodynamic integration based on an alchemical path linking the pure Al liquid to the Al-Sm liquid [28].

A semi-empirical potential describing the interatomic interaction in the Al-Sm system was taken from Ref. [29]. This FS potential is developed to accurately reproduce the Al-Sm properties including the pure Al melting temperature and formation energies of the Al-Sm crystal phases. Previous studies have shown that this potential well describes the AlSm liquid structure similar to the *ab inito* MD simulations [18, 30] and produces structure factors in good agreement with experimental measurements [31]. All MD simulations reported in the present paper were performed at $T = 700$ K using the *NPT* ensemble with Nose-Hoover thermostat. The time step of the simulation was 1.0 *fs*. The simulation cell contained 13,500 atoms and was at least 20 times larger than the critical nucleus size. The initial liquid was equilibrated for 1 *ns*. All the simulations were performed using the GPU-accelerated LAMMPS code [32–34].

To identify solid-like and liquid-like atoms during the MD simulation, the widely-used bond-orientational order (BOO) parameter [35, 36] was employed by calculating $S_{ij} = \sum_{m=-6}^{6} q_{6m}(i)\cdot q^*_{6m}(j)$ between two neighboring atoms based on the Steinhardt parameter $q_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\vec{r}_{ij})$, where $Y_{lm}(\vec{r}_{ij})$ is the spherical harmonics and $N_b(i)$ is the number of nearest neighbors of atom i. Two neighboring atoms i and j were considered to be connected when S_{ij} exceeds a threshold S_c. To choose a statistically sound threshold value, we plotted the population of mislabeled atoms in bulk Al liquid and crystal as a function of the threshold values in Fig. 1(a). The crossing point between the mislabeling curves of the liquid and solid phases was chosen as the threshold [25, 37]. With this threshold S_c, crystal and liquid can be well separated by counting the number of connections an atom has with its neighbors as shown in Fig. 1(b). We then used 6 as the connection cut-off to recognize solid-like atoms during the simulation [27]. The clustering analysis [38], which uses the crystalline bond length as the cutoff distance to choose neighbor atoms, is applied to measure the size of the nucleus formed during MD simulations. We examined the short-range order in the nucleus based on the packing motif of the atom cluster defined by the center atom and its nearest neighbor atoms. A cluster-alignment method [39] in which minimal root-mean-square deviations (RMSD) between the atom cluster and the perfect packing templates such as fcc, hcp and bcc polyhedra are calculated for crystal-structure recognition. The RMSD-based order parameter has been shown to be robust in characterization of the local structural ordering in the crystal, liquid and glasses [30, 40, 41].

In conventional MD simulation, the crystal nucleation is too rare event within the limited simulation time scales making it difficult to accurately measure the critical nucleus size except under extremely highly driven conditions [42]. The PEM allows efficient sampling of the nucleation process by preventing a small crystal embryo (with N_0 atoms which is much smaller than the critical nucleus) from melting using external spring forces [25]. This removes long periods of ineffective simulation where the system is very far away from forming a critical nucleus. As the embryo grows, the harmonic potential is gradually weakened and is completely removed when the cluster size reaches a sub-critical threshold N_{sc} ($<N^*$). During the simulation, the harmonic potential only applies to the original N_0($<N_{sc}$) embryo atoms. The spring constant of the harmonic potential can be expressed as $k(N) = k_0\frac{N_{sc}-N}{N_{sc}}$ if $N < N_{sc}$ and $k(N) = 0$, otherwise. This strategy ensures the system is unbiased at the critical point such that a reliable value of N^* is obtained. If the nucleus melts below N_{sc} ($<N^*$) the harmonic potential is gradually enforced preventing the complete melting of the embryo. When the nucleus reaches the critical size, it has equal chance to melt or to further grow causing critical fluctuations about N^*. Because the thermodynamic driving forces for growth or shrinking of the nucleus are smallest at the

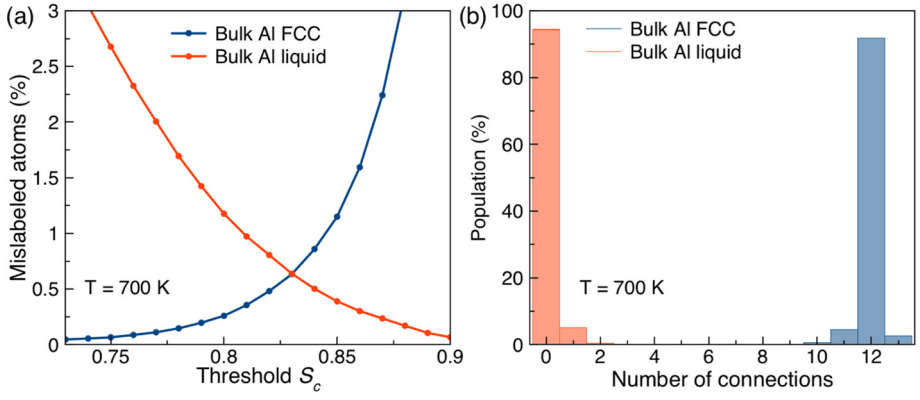

Fig. 1. Determination of the threshold to distinguish solid-like and liquid-like atoms. (a) Population of mislabeled atoms by different threshold values in bulk Al crystal and liquid at 700 K. (b) Population of connections number per atom in bulk Al crystal and liquid at 700 K.