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## Nucleation kinetics in Al-Sm metallic glasses

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### ABSTRACT

The isothermal nucleation kinetics in Al-Sm metallic glasses with low Sm concentrations ( $x_{Sm}$ ) was studied using molecular dynamics simulations in order to calculate time–temperature–transformation curves. The average delay time of Al nanocrystal nucleation was found to increase exponentially with  $x_{Sm}$ , whereas the estimated critical cooling rate necessary to avoid crystallization decreases exponentially with  $x_{Sm}$ . Sm solutes were found to suppress Al nucleation by increasing the attachment barrier and therefore by reducing the attachment frequency. The analysis shows that the attachment of Al to the evolving nucleus has the same characteristics as Al diffusion within the amorphous matrix and they both take place heterogeneously via collective movement of a group of Al atoms.

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### 1. Introduction

Metallic glasses (MGs) have attracted a growing interest since they were first reported in 1960 by Duwez et al. [1], due to their superior mechanical properties, better corrosion resistance and formability [2–5], as compared to their crystalline counterparts. In particular, Al-based MGs have a lower density and higher specific strength, and therefore have become promising candidates for applications as structural components [6,7]. Rapidly quenched Al-based MGs are usually characterized by a primary crystallization reaction upon heating which produces a high density of face-centered cubic (FCC) Al nanocrystals and consequently enhances the mechanical properties evidently [8–10]. For instance, it has been reported that the fracture strength of MGs with such nanocrystalline dispersions is 20–120% higher than that of the pure amorphous phase alloys with the same compositions [11–13].

The primary crystallization is of significant importance in understanding glass formation of alloys and there are two aspects of the primary crystallization that are still not well understood. One of them concerns unknown mechanisms underlying the effect of micro-alloying on the glass forming ability (GFA) of Al-based and other systems. This effect is known to be significant [14,15]. The second issue that needs to be elucidated is the nucleation kinetics in the primary crystallization [16], especially on the atomic level. To

address these issues, here molecular dynamics (MD) simulations were carried out to investigate the isothermal nucleation reactions of Al-Sm binary MG. This glass has been reported in experiments to undergo the primary crystallization during annealing [16–19]. In this study, a particular attention is devoted to Sm effect on the nucleation kinetics and the atomic-level mechanism controlling the nucleation attachment. Simulation of the crystal growth after the nucleation is outside the scope of this study.

### 2. Methods

MD simulations are performed using the LAMMPS simulation package [20], based on a Finnis-Sinclair type semi-empirical potential developed for Al-Sm alloy by Mendeleev et al. [21]. Although this potential has been fitted only to a limited number of properties during the development procedure, it has been shown to reproduce many properties that are relevant to the current study. These include the cohesive energy, melting temperature, and fusion enthalpy of pure Al, formation energies of Al-Sm crystal phases [21], and icosahedral ordering during rapid solidification of Al-Sm alloys [22]. In addition, this potential has been demonstrated to predict the same total and partial pair distribution functions as *ab initio* MD simulations in Al<sub>90</sub>Sm<sub>10</sub> liquid [21] and supercooled liquid [23], and produce structure factors in a reasonable agreement with experimental measurements in Al<sub>90</sub>Sm<sub>10</sub> MGs [23]. This potential is therefore generally suitable for simulating solidification/vitrification in Al-Sm system at low Sm concentrations.

In the simulations, a  $9 \times 9 \times 9 \text{ nm}^3$  simulation box was used,

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that contained a total of 42,592 atoms, and the periodic boundary conditions were enforced in all three Cartesian directions. An isothermal-isobaric (NPT) ensemble is used in all the simulations and the temperature and pressure are controlled with the Nose-Hoover thermostat and barostat, respectively. The nominal pressure is maintained to 0 GPa. The Al-Sm sample is prepared by randomly substituting a certain fraction of Al atoms with Sm atoms in the solid state. The sample is first heated to 2000 K in order to melt it, then it is equilibrated at this high temperature for 300 ps, followed by a rapid cooling ( $4 \times 10^{13}$  K/s) to 10 K to let the system vitrify. After an additional equilibration at 10 K, the as-quenched system is reheated quickly to the annealing temperature  $T_{\text{anneal}}$  for an isothermal nucleation reaction. The delay time  $\tau$  for the first nucleation event since the start of the annealing process is recorded in every annealing simulation. An adaptive common neighbor analysis method [24] was used for the structure identification, which examines the local environment to classify each atom as different structural types such as FCC, hexagonal close packed (HCP), body-centered cubic (BCC), or amorphous structure. Details of the temperature history, sample structural evolution, as well as the method to determine the delay time can be found in the [Supplemental Materials](#).

In order to understand the Sm effect on nucleation, the nucleation data was fitted with the classical nucleation theory (CNT). From these fits the nucleation kinetic barriers were determined and then compared with Al/Sm diffusion energy barriers in order to identify the controlling process in the Al nucleation kinetics. Diffusion coefficients are calculated in the pre-nucleation state of the MG (see the [Supplemental Materials](#)). The details are reported in [Secs. 3.2 and 3.3](#). Finally, the mechanisms participating in the nucleation event were identified; these mechanisms are compared to those governing Al diffusion in Al-Sm MG and are discussed in [Sec. 3.4](#).

One should note that, in this paper, the term “nucleation barrier” is avoided since it is ambiguous and does not distinguish the nucleation free energy barrier  $\Delta G^*$  from the nucleation kinetic barrier  $Q$ .  $\Delta G^*$  is the free energy cost associated with the formation of a critical nucleus of a new phase, whereas  $Q$  is the energy barrier per atom that needs to be overcome in the process of atomic attachment to nuclei.

### 3. Results

#### 3.1. Time–temperature–transformation (TTT) curves

Isothermal nucleation reactions were simulated for Al-Sm MGs with four Sm concentrations ( $x_{\text{Sm}} = 0.0, 1.0, 2.0$  and  $3.0$  at.%) at different  $T_{\text{anneal}}$ . The time step was set to 10 fs for 3.0 at.% and 2 fs otherwise. Ten independent simulations were run for each composition and each temperature. The average  $\tau$  and the corresponding error bars are plotted in [Fig. 1\(a\)](#). The measured delay times for different temperatures comprise the TTT curve that marks the onset of the crystallization transformation for each concentration. [Fig. 1\(a\)](#) shows that addition of Sm shifts the TTT curve towards the larger value of  $\tau$  and therefore it retards the primary crystallization and enhances GFA of Al-Sm MGs. The “nose” temperatures ( $T_{\text{nose}}$ ) of the TTT curves are in the range of  $0.48 T_m - 0.54 T_m$ , where  $T_m$  is the melting temperature (933 K) of pure Al. The cooling process starts at  $T_m$  and the temperature decreases linearly with time  $t$ , i.e.,  $T = 933 \text{ K} - R_c t$ . The corresponding continuous cooling curves tangential to the TTT curves at the “nose” temperature are also shown in [Fig. 1\(a\)](#). Here,  $R_c$  is the estimated critical cooling rate. The estimated steady state nucleation rate  $J_s$  ( $J_s \approx e/(V\tau)$ ) was also calculated and it shows the opposite trend

with temperature and Sm concentration (see [Fig. S3 in Supplemental Materials](#)).

To determine quantitatively the effect of Sm on the nucleation delay time  $\tau$ , we anneal the systems at a fixed  $T/T_g$  ratio of 0.95. Here the glass transition temperature,  $T_g$ , is calculated with the method described in [Refs. \[21\] and \[25\]](#), and the calculated values of  $T_g$  are shown in [Table 1](#). The ratio of 0.95 is chosen because typical annealing experiments of Al-based MG use similar ratios [18,19].  $\tau$  as a function of  $x_{\text{Sm}}$  is plotted in [Fig. 1\(b\)](#). Apart from the previously mentioned four Sm concentrations, simulations with 0.5 at.% and 1.5 at.% concentrations are also performed and reported here. The increasing trend of  $\tau$  with  $x_{\text{Sm}}$  can be fitted with the power law:  $\tau = C \cdot 10^{kx_{\text{Sm}}}$ , where  $C = 0.228$  ns and  $k = 0.787$ . The mechanism underlying this significant effect of Sm on  $\tau$  will be discussed in [Secs. 3.2 and 3.3](#). The fact that the error bar of  $\tau$  (note the logarithmic scale) increases with  $x_{\text{Sm}}$  implies a more stochastic nature of the nucleation process at higher Sm concentrations.

The critical cooling rate  $R_c$  as a function of  $x_{\text{Sm}}$  is plotted in [Fig. 1\(c\)](#). It is found that the decay of  $R_c$  with increasing  $x_{\text{Sm}}$  is well approximated by a power function, i.e.,  $R_c = C' \cdot 10^{-k'x_{\text{Sm}}}$ , where  $C' = (9.9 \pm 3.8) \times 10^{12}$  K/s and  $k' = 0.96 \pm 0.09$ . Our predictions are in a good agreement with available literature data. For instance, MD simulations by Hou et al. [26] with an embedded atom method interatomic potential [27] have shown that  $R_c$  for pure Al is within the range of  $4.0 \times 10^{12} - 1.0 \times 10^{13}$  K/s. This result is consistent with that of  $6.8 \times 10^{12}$  K/s found in our work. On the other hand, if the power relation determined in our simulations is extrapolated to higher  $x_{\text{Sm}}$ ,  $R_c$  is predicted to be  $2.24 \times 10^4 - 1.59 \times 10^6$  K/s for  $x_{\text{Sm}} = 8.0$  at.%, which corresponds to the composition of a well-known marginal glass former [9,10]. This predicted range is consistent with experimental data [28,29], which showed that general Al-based MGs have  $R_c$  in the range of  $10^4 - 10^6$  K/s.

#### 3.2. Nucleation kinetics

In order to understand the Sm effect on the nucleation kinetics, our simulation data was evaluated in the light of the CNT for homogeneous nucleation. From CNT, the steady-state nucleation rate  $J_s$ , defined as the number of nuclei in unit volume per unit time, can be written as [30,31].

$$J_s = \omega^* Z N^* \quad (1)$$

where  $\omega^*$ ,  $Z$  and  $N^*$  are the attachment frequency of monomers to the critical nucleus, the Zeldovich factor, and the equilibrium concentration of critical nuclei, respectively.  $\omega^*$  and  $N^*$  represent the kinetic and thermodynamic contributions, respectively, to the overall nucleation rate, and they can be calculated as

$$\omega^* = AC\nu\lambda \exp\left(-\frac{Q}{k_B T}\right), \quad (2)$$

$$N^* = N_1 \exp\left(-\frac{\Delta G^*}{k_B T}\right). \quad (3)$$

Here,  $A$  is the nucleus surface area,  $C$  is the concentration expressed in number of monomers per volume,  $\nu$  is a frequency factor,  $\lambda$  is the mean free path of Al in MG,  $N_1$  is Al monomer concentration,  $T$  is temperature,  $k_B$  is the Boltzmann constant,  $Q$  is the nucleation kinetic barrier, and  $\Delta G^*$  is the free energy barrier determined by nucleation driving force  $\Delta G_v$  and interfacial energy  $\gamma$  [31]. For spherical nuclei,  $\Delta G^* = 16\pi\gamma^3/(3\Delta G_v^2)$  [32].

Nucleation is controlled by thermodynamics at shallow

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