

Full length article

Nucleation kinetics in Al-Sm metallic glasses



L. Zhao, G.B. Bokas, J.H. Perepezko, I. Szlufarska*

Department of Materials Science and Engineering, University of Wisconsin, Madison, United States

ARTICLE INFO

Article history:

Received 10 August 2017
 Received in revised form
 20 September 2017
 Accepted 21 September 2017
 Available online 23 September 2017

Keywords:

Metallic glass
 Nucleation
 Delay time
 Attachment
 Molecular dynamics

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.

© 2017 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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 Mendelev 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 Al₉₀Sm₁₀ liquid [21] and supercooled liquid [23], and produce structure factors in a reasonable agreement with experimental measurements in Al₉₀Sm₁₀ 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,

* Corresponding author.

E-mail address: szlufarska@wisc.edu (I. Szlufarska).

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 (4×10^{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_{anneal} for an isothermal nucleation reaction. The delay time τ 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 ΔG^* from the nucleation kinetic barrier Q . ΔG^* 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_{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 τ 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 τ and therefore it retards the primary crystallization and enhances GFA of Al-Sm MGs. The “nose” temperatures (T_{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 τ , 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]. τ as a function of x_{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 τ with x_{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 τ will be discussed in [Secs. 3.2 and 3.3](#). The fact that the error bar of τ (note the logarithmic scale) increases with x_{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_{Sm} is plotted in [Fig. 1\(c\)](#). It is found that the decay of R_c with increasing x_{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 6.8×10^{12} K/s found in our work. On the other hand, if the power relation determined in our simulations is extrapolated to higher x_{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 ω^* , Z and N^* are the attachment frequency of monomers to the critical nucleus, the Zeldovich factor, and the equilibrium concentration of critical nuclei, respectively. ω^* 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, ν is a frequency factor, λ 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 ΔG^* is the free energy barrier determined by nucleation driving force ΔG_v and interfacial energy γ [31]. For spherical nuclei, $\Delta G^* = 16\pi\gamma^3/(3\Delta G_v^2)$ [32].

Nucleation is controlled by thermodynamics at shallow

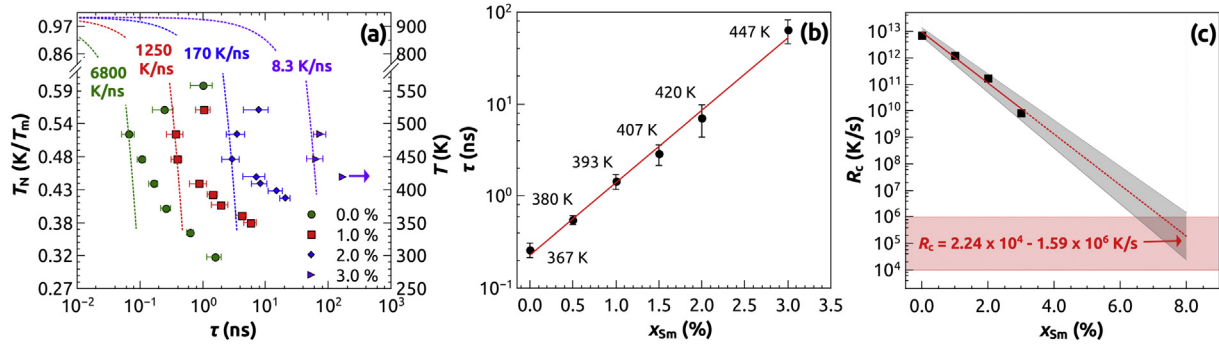


Fig. 1. (a) TTT curves for $x_{Sm} = 0.0$ at.% (green circle), 1.0 at.% (red rectangle), 2.0 at.% (blue diamond) and 3.0 at.% (violet right triangle). T_N represents the homologous temperature T/T_m . The standard deviation is shown as the error bar. The continuous cooling curves are plotted as dashed lines and the values of R_c are indicated. (b) Delay time τ as a function of x_{Sm} at $0.95 T_g$. The solid line is the exponential fitting. (c) Critical cooling rate R_c as a function of x_{Sm} . The data is fitted with the power relation and extrapolated to higher x_{Sm} . The grey and red areas represent the fitting error bar and the reported range of R_c for marginal glass formers, respectively. The predicted range of R_c for $x_{Sm} = 8.0$ at.% is $2.2 \times 10^4 - 1.6 \times 10^6$ K/s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1

Calculated T_g and T_{anneal} ($T_{anneal} = 0.95 T_g$).

x_{Sm} (at.%)	T_g (K)	T_{anneal} (K)
0.0	386	367
0.5	400	380
1.0	414	393
1.5	428	407
2.0	442	420
3.0	471	447

supercoolings ($T > T_{nose}$) due to the smaller nucleation driving force and it is controlled by kinetics at deep supercoolings ($T < T_{nose}$) due to the slower atomic mobility. The balance of these thermodynamic and kinetic factors results in the highest nucleation rate at T_{nose} . In our simulations a number of sub-critical Al FCC clusters have been observed at deep supercoolings, and their formation is due to the high nucleation driving force. However, these sub-critical clusters grow very slowly and very few of them have a chance to grow to the super-critical size, indicating a sluggish nucleus attachment kinetics and resulting in the prolonged delay time at deep supercoolings. Therefore, at $T < T_{nose}$, the term $\exp(-Q/k_B T)$ dominates,

and Eq. (1) can be rewritten as $J_s = K \exp(-Q/k_B T)$ with K as approximately constant. Since the delay time τ is inversely proportional to J_s [33], therefore, one can write $\tau \propto \exp(Q/k_B T)$.

Fig. 2 plots $\ln(\tau)$ vs. $1/T$ in the temperature range of $T < T_{nose}$, along with the fits. The nucleation kinetic barrier Q_i is calculated as $Q_i = k_i k_B$, where k_i is the slope of the fitting line. The values of Q for $x_{Sm} = 0.0, 1.0$ and 2.0 at.% are 0.208 ± 0.017 , 0.379 ± 0.040 and 0.531 ± 0.098 eV, respectively. Note that Q for 2.0 at.% Sm concentration has a large error bar, because the long nucleation delay time restricts the temperature range that can be studied for this concentration. Clearly, Sm additions raise the nucleation kinetic barrier Q and therefore they significantly reduce the Al attachment rate ω^* to nuclei. As a result, the nucleation delay time increases exponentially with increasing Sm as shown in Fig. 1(b).

3.3. Rate-limiting process in nucleation

Having shown that Sm solutes remarkably reduce the frequency of Al attachment to nuclei, an interesting question that arises is what is the controlling process in Al nucleation kinetics. It has been shown that the atomic transport in nucleation can be governed either by bulk diffusion or by interface attachment, depending on specific circumstances [34–36].

In order to discover the process controlling the development of Al nucleus, we calculate the diffusion energy barriers (E_{Al} and E_{Sm} for Al and Sm, respectively) and compare them with the nucleation attachment barrier Q . E_{Al} and E_{Sm} are obtained by fitting the diffusion coefficients determined during annealing before any nucleation took place. Details on the calculation of diffusion coefficients and diffusion energy barriers can be found in the Supplemental Materials. The nucleation kinetic barrier (Q) and the diffusion energy barriers (E_{Al} and E_{Sm}) are plotted together in Fig. 3 for comparison. The fact that the nucleation kinetic barrier Q is smaller than E_{Sm} indicates that the attachment frequency is controlled by a process that is faster than Sm bulk diffusion. There is a relatively good overall agreement between Q and E_{Al} , which in principle might mean that Al diffusion is the rate controlling process. However, this is not a valid explanation because the Sm concentration is very low and the prevalence of Al atoms near nuclei makes the long-distance diffusion of Al unnecessary for nucleation. This analysis implies that the attachment frequency is interface-controlled and Al atomic transfer across the interface (constituting an “attachment” event) is the rate limiting process in the composition range considered in this study.

It is interesting that the interface attachment of Al to a nucleus

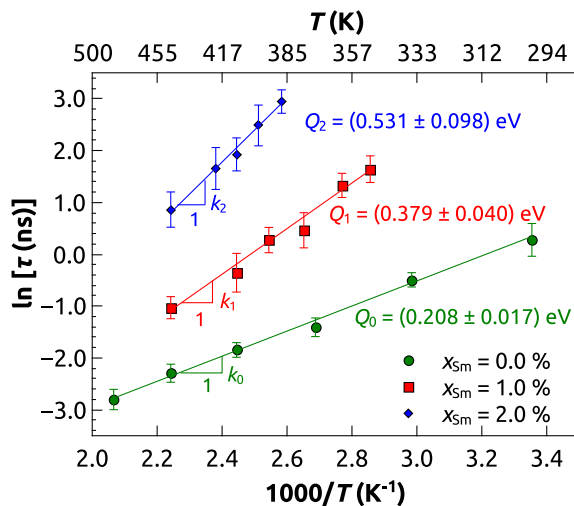


Fig. 2. $\ln(\tau)$ vs. $1/T$ for $T < T_{nose}$. The solid lines are the weighted exponential fitting of delay time τ . The nucleation kinetic barrier Q_i is calculated as $Q_i = k_i k_B$, where k_i represents the slope of the fitting line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

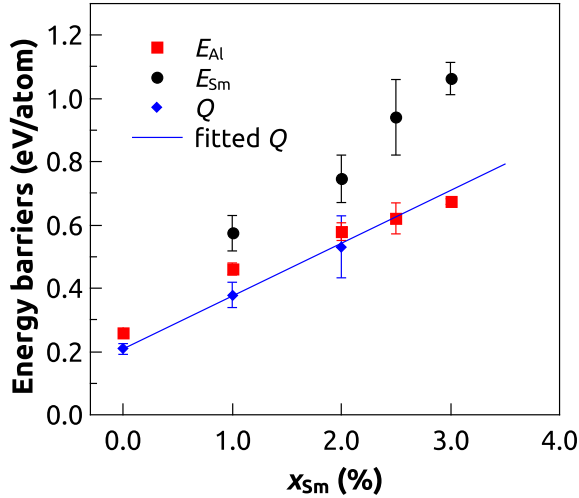


Fig. 3. Nucleation kinetic barrier (Q) and diffusion energy barriers (E_{Al} and E_{Sm}). The sizes of the error bars represent standard deviations in the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

would have a comparable energy barrier to the barrier for Al diffusion through the bulk MG. In order to shed light on this observation, the specific mechanisms underlying both Al diffusion and attachment will be examined and compared to each other in the following section.

3.4. Diffusion and nucleation attachment mechanism

Unlike crystalline metals where diffusion often occurs by means of single-atom jumps via a vacancy or interstitial mechanism, MD simulations have shown that diffusion in many MGs takes place in a heterogeneous manner (i.e., in a given time interval there are diffusing and non-diffusing regions of the structure) and that diffusion occurs through collective movement of a chain or ring of atoms [37,38]. Here, first a quantitative analysis was conducted for the simulated samples to confirm that Al diffusion in our system follows the same collective pattern as reported in many other MGs [37,38]. Then it will be shown that during nucleation, attachment of Al atoms to nuclei is also heterogeneous and involves a collective motion of atoms.

3.4.1. Al diffusion mechanism

To elucidate the diffusion mechanism in MGs, it is first necessary to identify the diffusing atoms (DAs) and the diffusion events. Here, the DAs are defined as those which perform displacements larger than a cut-off d_c within a time window Δt . All the DAs identified in this section are Al atoms, as Sm atoms displace too slowly and are not diffusing by the cut-off definition. In fact, the diffusion coefficient of Sm atoms is at least one order of magnitude lower than that of Al, as shown in Fig. S4 in Supplemental Materials. The fraction of DAs among all the atoms in the sample is usually smaller than a few percent and it decreases with increasing d_c and decreasing Δt . The number and fraction of DAs for different d_c and Δt can be found in Fig. S5 in the Supplemental Materials. Once the DAs have been identified, the spatial correlations among these atoms are analyzed to address the question of whether Al diffusion is heterogeneous. For this purpose, the nearest neighbor analysis (NNA) and reduced number density analysis are employed on all the DAs.

In NNA, the average distance d_{nn} between the nearest neighboring DAs is first calculated. The nearest neighbor index (NNI) is then defined as d_{nn}/d_{ran} , where $d_{ran} = 0.55396N_v^{-1/3}$ is the theoretical average nearest neighbor distance for the same number of randomly distributed atoms [39]. From NNI one can learn whether the DAs are clustered ($NNI < 1$), randomly distributed ($NNI \approx 1$), or more uniformly distributed than random ($NNI > 1$). Fig. 4(a) shows an example of a calculated NNI for a relaxed system with $x_{Sm} = 2.0$ at.% and $T = 0.95 T_g$ before nucleation occurs. Since $NNI < 1$, this means the DAs tend to cluster and they perform diffusing displacements collectively. Different choices of Δt lead to qualitatively the same results. Fig. 4(b) presents a 2D view of DAs for $d_c = 2.5$ Å and $\Delta t = 100$ ps. This analysis shows that the distribution of DAs is highly heterogeneous and that DAs form chains or rings, confirming the cooperative nature of Al diffusion.

In addition to NNA, the reduced number density ρ/ρ_0 of DAs was also calculated. Here, ρ is the number density of DAs around the central DA and is calculated as $\rho = N(r)/(\frac{4}{3}\pi r^3)$, where $N(r)$ is the DA count within a distance r from the central DA. ρ_0 is the average number density of DAs in the system. Fig. 4(c) shows ρ/ρ_0 of DAs for different Sm concentrations at $T = 0.95 T_g$ using $d_c = 2.5$ Å and $\Delta t = 60$ ps. It is evident that ρ/ρ_0 increases with decreasing r and reaches a maximum value at around the nearest Al-Al distance, which indicates that the DAs are prone to become direct nearest neighbors of each other. This is consistent with the observation in Fig. 4(b). The decrease of ρ/ρ_0 with increasing Sm concentration suggests the decreasing size of the DA-cluster. This trend is

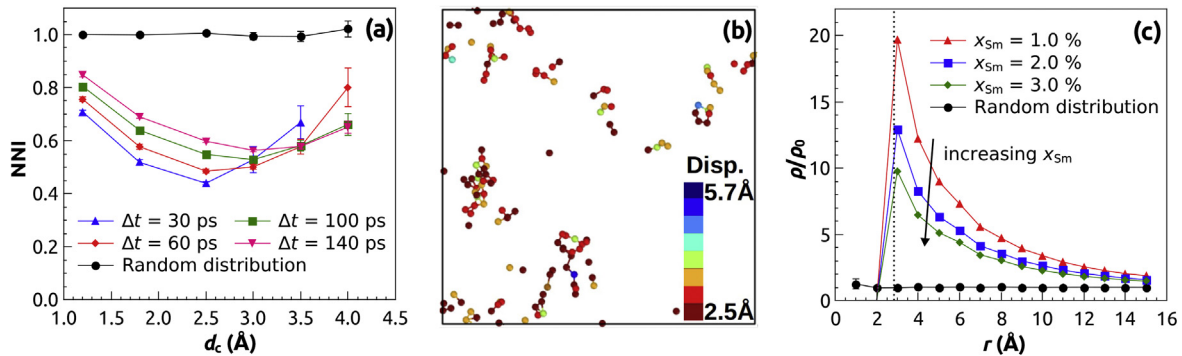


Fig. 4. (a) NNI of DAs as a function of displacement cut-off d_c and time window Δt . (b) A 1-nm-thick 2D slice of the DAs for $d_c = 2.5$ Å and $\Delta t = 100$ ps. The color represents displacement magnitude. (c) Reduced number density of DAs around the central DA. Here $d_c = 2.5$ Å and $\Delta t = 60$ ps are used to define diffusing events. The vertical dashed line represents the nearest Al-Al distance (2.8 Å) in the system. (a) and (b) are obtained from the system with $x_{Sm} = 2.0$ at.%. For comparison, in (a) and (c), respectively, we also plot NNI and the reduced number density for randomly distributed atoms with the same number of atoms as DAs in our Al-Sm samples. In (c) the data corresponds to $\Delta t = 60$ ps. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

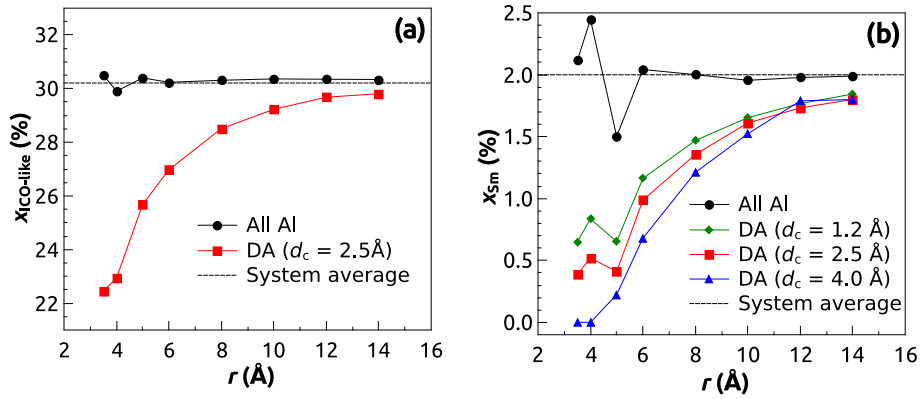


Fig. 5. (a) ICO-like VP concentration $x_{\text{ICO-like}}$ and (b) Sm concentration x_{Sm} around the central diffusing Al atom (DA). These concentrations around any Al atom and the system average concentrations are also plotted for comparison. The diffusing events are defined using $\Delta t = 100$ ps and different d_c . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

attributed to the reduced size of the liquidlike diffusion channels with increasing Sm concentration, as discussed later in this section.

To elucidate further the collective nature of DAs, their spatial correlations are analyzed with the icosahedral Voronoi polyhedra (ICO VP) and Sm atoms. The motivation for this analysis is that the concentration of ICO VPs has been previously argued to be correlated with the GFA of an alloy [40,41]. In this case, the ICO VPs are identified by applying the Voronoi tessellation technique [42] and then grouped based on their Voronoi indices [22]. The concentrations of the center atoms of ICO-like VPs and Sm atoms within a distance r from any DA are calculated and plotted in Fig. 5(a) and (b), respectively. According to Fig. 5(a) there are fewer ICO-like VPs near DAs, implying that DAs tend to avoid ICO VPs. This observation is consistent with findings previously reported in literature. Specifically, Zhang et al. [38] reported that the diffusion of Cu in a Cu-Zr MG is confined in the liquidlike regions that are poor in icosahedral short-range order, and Bokas et al. [22] found that in Al-Sm MGs the diffusion coefficient of Al with ICO-like VP is one order of magnitude lower than other Al atoms at low Sm concentration range. In the same vein, Fig. 5(b) shows that DAs are prone to avoid Sm atoms

in the sample and that faster DAs (i.e., DAs that have larger displacements within a fixed time window) have stronger avoidance tendency. We speculate that Sm can have an important effect on Al diffusion by increasing the fraction of ICO-like VPs [22]. This would take place not only because Sm increases the fraction of Al-centered ICO-like VPs, but also because most of the Sm-centered clusters are ICO-like. As a result, the average size of liquidlike channels is reduced and it takes a longer time for Al atoms to navigate the torturous diffusion paths inside the narrower channels. Finally, the fact that the sizes of liquidlike channels and DA-clusters correlate with each other explains the decreasing size of DA-clusters with increasing x_{Sm} , as shown in Fig. 4(c).

3.4.2. Nucleation attachment mechanism

In order to illustrate the mechanism of Al attachment during nucleation, Fig. 6 presents the snapshots of Al attachment process during the growth of a nucleus in the system with $x_{\text{Sm}} = 2.0$ at.% and $T = 0.95 T_g$. In the first image, the grey atoms are the original FCC atoms at $t = 0$ ps and they are used to construct an isosurface shown also in grey. In the following images (at longer times), only newly attached atoms are shown explicitly, and the colors and arrows, respectively, represent the magnitude and the direction of the atom's displacement relative to its position at $t = 0$ ps. From the images shown in Fig. 6, one can see that the attachment is heterogeneous in space and atoms tend to attach to nuclei collectively as a cluster. Examples of these clusters are marked with the blue ellipses in the images in Fig. 6.

The attachment is not only heterogeneous in space, but also in time. The temporal heterogeneity of attachment was verified by tracking the dynamic fluctuation of the instantaneous net increase N_{net} of the number of atoms added to the nucleus within the period of 10 ps, i.e., $N_{\text{net}} = N_{\text{att}} - N_{\text{det}}$, where N_{att} and N_{det} are the instantaneous numbers of attachment and detachment events within 10 ps, respectively. Fig. 7 shows N_{net} vs. time t for a nucleus growing from 17 atoms to 189 atoms within 3.7 ns; during this time there are in total 4757 attachment events and 4585 detachment events. One can see that N_{net} exhibits strong fluctuations, which indicates the temporal heterogeneity of the nucleus growth. To further demonstrate this temporal heterogeneity, the simulation method was modified to numerically model a randomized nucleus growth. For the analysis, the following simplifying assumptions were made: 1) The nucleus is spherical and the nucleus surface area $A = (4\pi)^{1/3}(3NV_0)^{2/3}$, where N and V_0 are the number of nucleus atoms and the atomic volume, respectively; 2) the probability of attachment and detachment at any time is proportional to the nucleus

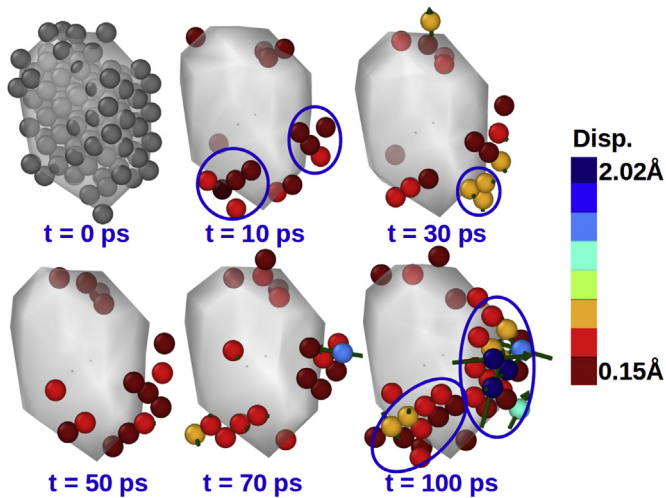


Fig. 6. Nucleus attachment process for $x_{\text{Sm}} = 2.0$ at.% and $T = 0.95 T_g$. The isosurface represents the original nucleus surface at $t = 0$ ps. The color atoms are those that attach to nucleus subsequently. Color of the atoms and arrow represent the magnitude and direction of the displacement vector of a given atom. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

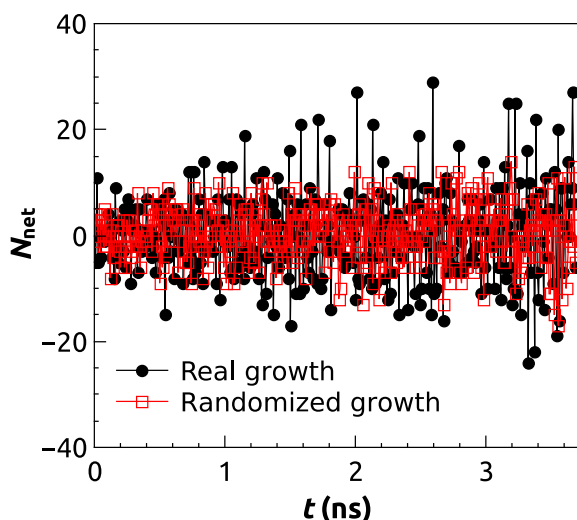


Fig. 7. The instantaneous net increase, N_{net} , of the number of atoms in the nucleus within 10 ps for real and randomized nucleus growth. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

surface area; and 3) the numbers of attachment and detachment events are the same as found in the full MD simulations with $x_{\text{Sm}} = 2.0$ at.% and $T = 0.95 T_g$, i.e., $N_{\text{att}} = 4757$ and $N_{\text{det}} = 4585$. The randomized fluctuation of N_{net} based on single-atom attachment/detachment is also plotted in Fig. 7. Clearly, the N_{net} fluctuation amplitude in randomized nucleus growth is much smaller than in the case of the real nucleus growth. This means that attachment of atoms to nuclei in a real system is not random and it is heterogeneous in time. The difference in N_{net} fluctuation in Fig. 7 can be attributed to the different nucleus growth modes (i.e., single atom attachment versus collective attachment) in these two systems.

In summary, our analysis shows that both Al diffusion and Al nucleation attachment occur highly heterogeneously via collective movements of a group of atoms. The common features of these physical processes may explain why the kinetic barrier Q of Al nucleation is comparable to the activation barrier E_{Al} of Al diffusion, as shown in Fig. 3.

4. Discussion

It has been suggested [43] that the homogeneous nucleation delay time τ is inversely proportional to the atomic attachment rate to nucleus, that is, $\tau \propto 1/\omega^*$. Combining the power law of τ (see Fig. 1(b)) and Eq. (2), taking the logarithm of both sides, and omitting constant terms, one can find that $Q \propto x_{\text{Sm}}$. This analysis is consistent with data shown in Fig. 3, where the dependence of the mean value of the attachment kinetic barrier Q on Sm concentration x_{Sm} can be well approximated by a linear function (despite the large error bar of Q at higher concentrations). This consistence implies a good agreement between our simulations and the theory.

Our simulation results show that, in the composition range (0.0–3.0 at.% Sm) studied, the nucleation kinetics in Al–Sm MG is governed by the interfacial attachment process. Mechanisms underlying Al interfacial attachment and Al diffusion share critical atomic-level features, i.e., they both occur heterogeneously through collective movements of a group of atoms. The fact that the nucleation kinetic barrier Q is smaller than E_{Sm} , as seen in Fig. 3, suggests that the bulk diffusion of Sm is not involved in the nucleation process. As the Sm concentration is low, most Sm atoms

might be transported away from the nucleus via the local rearrangement between Sm and Al atoms, while others are incorporated into the nucleus. The dominant role of the interfacial attachment mechanism might not hold true for nucleation at high Sm concentration or in the crystal growth regime (past the critical nucleus radius). In those cases it is possible that a Sm-rich shell is formed around Al nucleus/crystal interface and thereby the diffusion of Sm away from the nucleus/crystal interface might be expected to play the dominant role, as has been suggested in Refs. [10,44]. Further studies are needed to confirm the role of solute diffusion in the nucleation kinetics for high solute concentrations and for longer time.

Although it has been shown that Al nucleation attachment occurs highly heterogeneously via collective movements of a group of atoms, such a collective attachment mechanism violates CNT which assumes the nucleus growth is continuous via single atom attachment. However, the application of CNT to extract the nucleation kinetic barrier Q in Eq. (2) can still be justified, since Q would represent the average kinetic barrier per atom in the collective attachment.

5. Conclusion

The isothermal nucleation kinetics in Al–Sm MG was studied with x_{Sm} in the range of 0.0–3.0 at.%. The following general conclusions can be drawn from the results of our MD simulations:

- (1) Sm solutes significantly suppress the primary crystallization transformation in Al–Sm MG and thereby they enhance its glass formability. In particular, the nucleation delay time increases exponentially with x_{Sm} at a constant T/T_g ratio, whereas the critical cooling rate R_c decays exponentially with x_{Sm} . In addition, a reasonable range of R_c (2.24×10^4 – 1.59×10^6 K/s) has been predicted for $\text{Al}_{92}\text{Sm}_8$, which is a well-known marginal glass former.
- (2) Sm solute retards Al nucleation by increasing the nucleation kinetic barrier (and therefore by reducing the nucleus attachment rate). In the composition range considered in this study, the nucleation kinetics is controlled by interfacial attachments, rather than by Sm diffusion.
- (3) Similarly to Al diffusion in MGs, attachment of Al to a crystalline nucleus takes place heterogeneously in both space and time via the collective movement of a group of atoms. The common atomic-level processes between Al attachment and Al diffusion is consistent with the two processes having comparable activation energy barriers.

Acknowledgments

The authors are grateful to Dr. Ye Shen for helpful discussions of the critical cooling rates, and the Center for High Throughput Computing at University of Wisconsin, Madison for the computing resources. This work was supported by the NSF-DMREF under Grants DMR-1332851 and DMR-1728933.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.actamat.2017.09.050>.

References

- [1] W. Klement, R. Willens, P. Duwez, Non-crystalline structure in solidified gold–silicon alloys, *Nature* 187 (1960) 869–870.
- [2] A. Greer, K. Rutherford, I. Hutchings, Wear resistance of amorphous alloys and

- related materials, *Int. Mater. Rev.* 47 (2002) 87–112.
- [3] C.A. Schuh, T.C. Hufnagel, U. Ramamurty, Mechanical behavior of amorphous alloys, *Acta Mater* 55 (2007) 4067–4109.
 - [4] G. Kumar, H.X. Tang, J. Schroers, Nanomoulding with amorphous metals, *Nature* 457 (2009) 868–872.
 - [5] A. Inoue, A. Takeuchi, Recent development and application products of bulk glassy alloys, *Acta Mater* 59 (2011) 2243–2267.
 - [6] A. Inoue, K. Ohtera, A.-P. Tsai, H. Kimura, T. Masumoto, Glass transition behavior of Al-Y-Ni and Al-Ce-Ni amorphous alloys, *Jpn. J. Appl. Phys.* 27 (1988). L1579.
 - [7] Y. He, G. Dougherty, G. Shiflet, S. Poon, Unique metallic glass formability and ultra-high tensile strength in Al-Ni-Fe-Gd alloys, *Acta Metall. Mater* 41 (1993) 337–343.
 - [8] Y. He, S. Poon, G. Shiflet, Synthesis and properties of metallic glasses that contain aluminum, *Science* 241 (1988) 1640.
 - [9] J. Foley, D. Allen, J. Perepezko, Analysis of nanocrystal development in Al-Y-Fe and Al-Sm glasses, *Scr. Mater* 35 (1996) 655–660.
 - [10] G. Wilde, H. Sieber, J. Perepezko, Glass formation versus nanocrystallization in an Al92Sm8 alloy, *Scr. Mater* 40 (1999) 779–783.
 - [11] H. Chen, Y. He, G. Shiflet, S. Poon, Mechanical properties of partially crystallized aluminum based metallic glasses, *Scr. Metall. Mater* 25 (1991) 1421–1424.
 - [12] Y.-H. Kim, A. Inoue, T. Masumoto, Increase in mechanical strength of Al-Y-Ni amorphous alloys by dispersion of nanoscale fcc-Al particles, *Mater. Trans. JIM* 32 (1991a) 331–338.
 - [13] Y.-H. Kim, A. Inoue, T. Masumoto, Ultrahigh mechanical strengths of $\text{Al}_{88}\text{Y}_2\text{Ni}_{10-x}\text{M}_x$ ($\text{M} = \text{Mn, Fe or Co}$) amorphous alloys containing nanoscale fcc-Al particles, *Mater. Trans. JIM* 32 (1991b) 599–608.
 - [14] Z. Huang, J. Li, Q. Rao, Y. Zhou, Primary crystallization of Al-Ni-RE amorphous alloys with different type and content of RE, *Mater. Sci. Eng. A* 489 (2008a) 380–388.
 - [15] Z. Huang, J. Li, Q. Rao, Y. Zhou, Effects of replacing Ni by Co on the crystallization behaviors of Al-Ni-La amorphous alloys, *Intermet* 16 (2008b) 727–731.
 - [16] J. Perepezko, R. Wu, R. Hebert, G. Wilde, Synthesis and Stability of Amorphous Al Alloys, in: *MRS Proc.*, vol. 644, Camb. Univ. Press, 2000, pp. L4–L7.
 - [17] R. Wu, G. Wilde, J.H. Perepezko, Glass formation and primary nanocrystallization in Al-base metallic glasses, *Mater. Sci. Eng. A* 301 (2001) 12–17.
 - [18] J.H. Perepezko, R.J. Hebert, Amorphous aluminum alloys-synthesis and stability, *JOM* 54 (2002) 34–39.
 - [19] D. Allen, J. Foley, J. Perepezko, Nanocrystal development during primary crystallization of amorphous alloys, *Acta Mater* 46 (1998) 431–440.
 - [20] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comput. Phys.* 117 (1995) 1–19.
 - [21] M. Mendelev, F. Zhang, Z. Ye, Y. Sun, M. Nguyen, S. Wilson, C. Wang, K. Ho, Development of interatomic potentials appropriate for simulation of devitrification of Al90Sm10 alloy, *Model. Simul. Mater. Sci. Eng.* 23 (2015) 045013.
 - [22] G. Bokas, L. Zhao, J. Perepezko, I. Szlufarska, On the role of Sm in solidification of Al-Sm metallic glasses, *Scr. Mater* 124 (2016) 99–102.
 - [23] Y. Sun, Y. Zhang, F. Zhang, Z. Ye, Z. Ding, C.-Z. Wang, K.-M. Ho, Cooling rate dependence of structural order in Al90Sm10 metallic glass, *J. Appl. Phys.* 120 (2016) 015901.
 - [24] A. Stukowski, Structure identification methods for atomistic simulations of crystalline materials, *Model. Simul. Mater. Sci. Eng.* 20 (2012) 045021.
 - [25] M. Mendelev, M. Kramer, R. Ott, D. Sordelet, D. Yagodin, P. Popel, Development of suitable potentials for simulation of liquid and amorphous Cu-Zr alloys, *Philos. Mag.* 11 (2009) 967–987.
 - [26] Z. Hou, Z. Tian, R. Liu, K. Dong, A. Yu, Formation mechanism of bulk nanocrystalline aluminium with multiply twinned grains by liquid quenching: a molecular dynamics simulation study, *Comput. Mater. Sci.* 99 (2015) 256–261.
 - [27] M. Mendelev, M. Kramer, C.A. Becker, M. Asta, Analysis of semi-empirical interatomic potentials appropriate for simulation of crystalline and liquid Al and Cu, *Philos. Mag.* 88 (2008) 1723–1750.
 - [28] O. Senkov, D. Miracle, Effect of the atomic size distribution on glass forming ability of amorphous metallic alloys, *Mater. Res. Bull.* 36 (2001) 2183–2198.
 - [29] R. Suzuki, Y. Komatsu, K. Kobayashi, P. Shingu, Formation and crystallization of Al-Fe-Si amorphous alloys, *J. Mater. Sci.* 18 (1983) 1195–1201.
 - [30] A. Walton, Nucleation in liquids and solutions, *Nucleation* (1969) 225–307.
 - [31] I. Markov, Crystal growth for beginners: fundamentals of nucleation, *Cryst. Growth Epitaxy* (2003).
 - [32] F. Abraham, Homogeneous Nucleation: the Pretransition Theory of Vapor Condensation, 1974.
 - [33] J.A. Dantzig, M. Rappaz, Solidification, EPFL press, 2009.
 - [34] D. Kashchiev, Nucleation: Basic Theory with Applications, Butterworth-Heinemann, 2000.
 - [35] D. Kashchiev, G. Van Rosmalen, Review: nucleation in solutions revisited, *Cryst. Res. Technol.* 38 (2003) 555–574.
 - [36] M.A. Durán-Olivencia, J.F. Lutsko, Unification of classical nucleation theories via a unified Itô-Stratonovich stochastic equation, *Phys. Rev. E* 92 (2015) 032407.
 - [37] F. Faupel, W. Frank, M.-P. Macht, H. Mehrer, V. Naundorf, K. Rätzke, H.R. Schober, S.K. Sharma, H. Teichler, Diffusion in metallic glasses and supercooled melts, *Rev. Mod. Phys.* 75 (2003) 237.
 - [38] Y. Zhang, C. Wang, M. Mendelev, F. Zhang, M. Kramer, K. Ho, Diffusion in a Cu-Zr metallic glass studied by microsecond-scale molecular dynamics simulations, *Phys. Rev. B* 91 (2015) 180201.
 - [39] S. Chandrasekhar, Stochastic problems in physics and astronomy, *Rev. Mod. Phys.* 15 (1943) 1.
 - [40] Y. Cheng, E. Ma, H. Sheng, Alloying strongly influences the structure, dynamics, and glass forming ability of metallic supercooled liquids, *Appl. Phys. Lett.* 93 (2008) 111913.
 - [41] H. Peng, M. Li, W. Wang, C.-Z. Wang, K. Ho, Effect of local structures and atomic packing on glass forming ability in $\text{Cu}_{50}\text{Zr}_{50-x}$ metallic glasses, *Appl. Phys. Lett.* 96 (2010) 021901.
 - [42] J. Finney, Random Packings and the Structure of Simple Liquids. I. The Geometry of Random Close Packing, in: *Proc. R. Soc. Lond. A-math. Phys. Eng. Sci.*, vol. 319, The R. Soc, 1970, pp. 479–493.
 - [43] K.C. Russell, Nucleation in solids: the induction and steady state effects, *Adv. Colloid Interface Sci.* 13 (1980) 205–318.
 - [44] S. Imhoff, J. Ilavsky, F. Zhang, P. Jemian, P. Evans, J. Perepezko, Kinetic transition in the growth of Al nanocrystals in Al-Sm alloys, *J. Appl. Phys.* 111 (2012), 063525.