



Reassessing the atomic size effect on glass forming ability: Effect of atomic size difference on thermodynamics and kinetics



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ABSTRACT

Glass forming ability (GFA) for some alloys may be difficult to explain in kinetic point of view alone and the thermodynamics must be considered as an important factor. Herein, investigation of the atomic size effect on the glass forming ability based on the molecular dynamics simulations for binary alloys with Lennard-Jones Embedded Atom Method potentials have been performed. The findings from this study showed that the size effect is accompanied by the change of phase diagram from solid solution to eutectic and change in the local stress/internal energy, which could contribute more to GFA than the kinetic factors such as efficient packing and resulting sluggish atomic transport.

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1. Introduction

Since the first synthesis of an amorphous phase in the Au–Si binary system by the rapid solidification technique in 1960, numerous glass forming metallic alloys have been developed including bulk glass forming alloys [1]. The origin of the high stability of the amorphous structure against crystallization that enables glass forming ability (GFA) could be summarized in single phrase: ‘by the combination of thermodynamic and kinetic contributions.’ A more tangible explanation is given by Inoue’s empirical rules [2]. However, the key factors affecting GFA are still of interest to many researchers [3–5]. Among other factors, the atomic size difference perhaps constitutes the most basic principle for designing alloys with high GFA [6,7]. For example, one of the well-known empirical rules suggests that the atomic radii among alloy components should differ by more than 11% to form a glass. As

proposed by Polk [8], Lee [9], Li [3], and Miracle [5] the increase in the atomic size difference leads to an increase in the packing density of the system such that the supercooled liquid tends to have higher viscosity and lower diffusivity, leading to higher resistance against crystallization [10,11]. However, as recently addressed by Egami, glass stability is controlled by not only the stability of the glass itself, i.e. by efficient packing, but the instability of the competing crystalline phase [12,13]. His original work focuses on the effect of structural instability due to the local strain developed by atomic size differences, which controls the thermodynamic driving force to crystallization [12]. Thus, it is important to consider both factors: stability of the glass (i.e. the kinetics problem) and instability of the competing crystalline phase (i.e. the thermodynamics problem).

In this context, it is worth investigating the effect of atomic size difference on GFA by separating contributions from *kinetics* and *thermodynamics*. The outcome of kinetic and thermodynamic stabilization could be quite different. Kinetic stabilization would lead to glass brittleness and “strong” liquid behavior. Indeed, metallic glass-forming liquid exhibit a fairly wide range of “fragility” index [14–17].

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There have been many atomistic simulation studies on the effect of atomic size difference on the packing properties of randomly packed structure and glass forming ability using the model alloy systems with hard sphere or Lennard-Jones (LJ) potentials [18–22]. Recent work by Zhang et al. [21] reported based on their molecular dynamics (MD) simulations to compress binary hard spheres into jammed packing that there was a strong correlation between the GFA and packing density difference between the amorphous and random crystal structure, that is, more efficient packing induced better GFA. Zhang et al. [22] performed MD simulations of binary LJ mixtures and found that the best glass forming mixtures possess atomic size ratios less than 0.92 and stoichiometries near 50:50 by number. However, most atomistic researches mentioned above did not study the effect of atomic size difference on the GFA in the thermodynamic viewpoint such as the change of phase diagrams and the development of atomic distortions with varying atomic size ratios.

In this study, we utilized a model binary alloy (described by interatomic potentials of metallic bonding characteristics) to investigate the effect of atomic size difference on GFA. Kinetic and thermodynamic contributions are evaluated using molecular dynamics and Kofke phase diagram construction, respectively. GFA is quantitatively discussed in the context of classical nucleation theory.

2. Materials and methods

To overcome the current limitations of pair-wise potential models, we used an adjustable interatomic potential model: Lennard-Jones embedded-atom method (LJ-EAM) potential developed by Baskes [18,19]. The LJ-EAM model (refer to [Supplementary Information 1](#) for detailed description) is a simple extension of the Lennard-Jones (LJ) potential to account for the many-body bonding characteristics of metallic systems. Due to its simplicity, we can extract the general behavior of metallic glasses as a function of adjustable potential parameters such as atomic size and potential well-depth.

In the LJ-EAM model, we can combine the EAM form with the convenience of the adjustable LJ pair potential by choosing the pairwise term of the EAM formula in such a way that the total energy of the reference structure (here, face-centered cubic) as a function of dilation is described by a LJ potential formula. By matching the total energy curve to that of the LJ pair potential, we can define the effective LJ parameters such as the potential-well depth ϵ , and the LJ diameter σ . For unary metals, the total energy curves (as a function of dilation) were fitted to that of the face-centered cubic (fcc) structures of LJ models and for binary alloys, the total energy curves were fitted to that of the $L1_0$ alloy structures of LJ models. This could be a systematic way of defining effective atomic size in our model system.

We prepared a perfect face-centered cubic (fcc) lattice composed of 1372 atoms with randomly mixed A and B atoms, heated it up to 2400 K, well above its melting temperature ($T_m = 1161$ K) to ensure complete melting and then equilibrated it for a long period of more than 200 ps. Then, the system was quenched down to 0 K at various cooling rates of 2×10^{13} – 1×10^{11} K/s to simulate liquid-to-glass transition and during quenching we monitored its structure using bond-orientational order parameter Q_6 to determine the degree of disorder of atomic bonding configuration [19]. All the simulations were performed with a constant number of atoms (N) and constant pressure (P) and temperature (T), i.e. the NPT ensemble.

We have performed molecular dynamics (MD) simulations of liquid-to-glass transition for a set of model binary alloys with variation of atomic size and composition. The binary alloy has a

negative heat of mixing to encourage uniform mixing of different elements: $E_{AB}/E_{AA} = 1.1$ and $E_{AA} = E_{BB}$, where E_{AB} is the bonding energy between A and B. The potential parameters are fitted to reproduce the elastic properties of nickel. The potential parameters used for both atoms, A and B, are identical with the only exception of atomic size. We consider five model binary alloys with the atomic size ratios $\lambda = \sigma_B/\sigma_A = 0.8, 0.85, 0.9, 0.95,$ and 1.0 , where σ_A and σ_B are Lennard-Jones diameters of type A (larger atom) and type B (smaller atom), respectively.

2.1. Calculating packing density of alloys

To measure the packing density as shown in Fig. 1(b), three different atomic configurations of the liquid state at 2400 K were adopted and quenched down to 300 K with a cooling rate of 2×10^{13} K/s. After the stabilization of an amorphous phase at 300 K for ~ 1 ns, the packing density was obtained as $\rho = (N_{atoms} \times V_{atom})/V_{cell}$, where N_{atoms} is the total number of atoms, V_{atom} is the atomic volume, and V_{cell} is the volume of entire cell.

2.2. Evaluation of diffusivity

The diffusivity, D , of individual atoms can be estimated from the

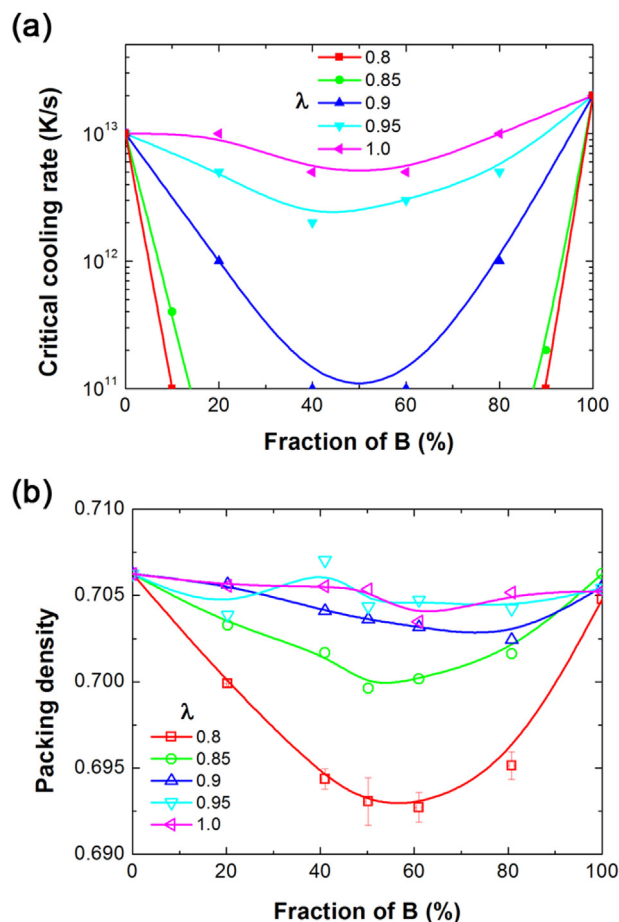


Fig. 1. Correlation of glass forming ability and packing density with atomic size difference. (a) Variation of critical cooling rate (K/s) with the fraction of B atoms for several different atomic size ratios. The critical cooling rate is defined as the lowest cooling rate at which crystallization is avoided. (b) Variation of packing density with the fraction of B atoms for several different atomic size ratios. Each packing density was obtained on the average of three different atomic configurations.

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