Prediction Optimum Composition for Glass Forming Ability of Bulk Amorphous Alloys: Application to Cu-Zr-Al

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Support Information

S1. Details of MD Simulations

All simulations are carried out using Lammps codes.[1] The energies and forces are determined using a recently developed embedded-atom model (EAM) potential[2] for Cu-Zr-Al ternary alloys. We started with our previous $Cu_{46}Zr_{54}$ glass model[3] which contains 8,640 Zr atoms and 7,360 Cu atoms. Then the Zr atoms were gradually substituted with Al atoms, leading to compositions of $Zr_{54-x}Cu_{46}Al_x$ (x = 1~25). The Zr atoms were replaced every 1% for Al concentration less than 10% and every 2.5% for greater than 10%. Periodic boundary conditions were applied in all three directions of the simulation box to eliminate surface effects. The equations of motion were solved using the velocity Verlet algorithm with a time step of 1 fs. The dynamics were carried with three sets of conditions:

- The NPT ensemble (constant particles [N], pressure [P] and temperature [T]),
- The NVT ensemble (constant particles [N], volume [V] and temperature [T]),
- The NVE ensemble (constant particles [N], volume [V] and energy [E])

using Nose-Hoover thermostat (time constant of 0.1 ps) and barostat (time constant of 1 ps). These compositions ($Cu_{46}Zr_{54-x}Al_x$) were heated at a uniform rate from 298K to 2,000 K using NPT at 0 atmosphere pressure MD for 2 ns; then we equilibrate the systems at 2000 K for 5 ns of NPT. Finally these equilibrated, liquids were quenched to room temperature (298 K) with the same cooling rate of $5x10^{11}$ K/s using NPT MD (at zero pressure).

S2. Thermodynamic driving force from two phase model

In order to extract such thermodynamics variables as entropy and free energy, we apply the two-phase thermodynamics (2PT) Density of States model, 2PT-DoS,[4-7] which extracts the vibrational density of states, DoS(ν) from the Fourier transform of the velocity autocorrelations function form NVT MD trajectory (requiring ~20 ps of MD). Since the Dos(ν) ≠ 0 at ν = 0, the 2PT model partitions this DOS into a diffusional part that has a finite value at ν = 0, with a form based on a gas of hard spheres, plus a solid part for which Dos(ν) ➔ 0 as ν ➔ 0. The entropy and free energy are extracted by integrating the energy expression of the thermodynamic variables over the modes as described in ref. [4-7]. We have validated this approach on various systems from CuZr, NiAl metallic system[4] to complex molecular and polymer systems.[6, 7]

We used these methods to extract the entropy and free energy of the liquid and crystal phases at temperatures slightly above T_g for various Al concentrations. We use the free energy of the liquid phase and crystal phases to extract the thermo dynamical driving force ΔG at T_g. We obtain undercooled liquid configurations from the quenching simulations.

In equilibrium, the crystal phases for various Al concentrations would have a mixture of 2 or 3 distinct crystal phases, but the time scales of our MD are too short for these phases to form in our simulations. Thus to extract the free energy of the mixed crystal phase, we start from the

known single crystal phases for various compositions and extract the free energy of these phases using our 2PT model. Then we apply the common tangent rule to obtain the optimum ratio for each single crystal component. Finally, the free energy of the mixing phases is extracted by adding the values of single phases at the optimum rations.

For the CuZr crystal (space group: Pm-3m) structure, we started with a 10×10×10 supercell (2000 atoms total) and substituted 4% Cu atoms with Zr atoms randomly, which we did independently 100 times. For each of the 100 structures, we optimize atomic coordinates using conjugate gradients and selected the lowest energy as the crystal structure for $Cu_{46}Zr_{54}$.

Then we randomly substituted 1% Zr atoms with Al atoms using the $Cu_{46}Zr_{54}$ crystal structure obtained from the previous step. Again this was done 100 times. These new structures were in turn minimized and the lowest energy structure was selected for the $Cu_{46}Zr_{53}Al_1$ crystal structure. We repeated the above procedure to obtain the crystal structures for all Al concentrations from 0% to 25%.

The Cu_2ZrAl (space group: Fd-3m) and CuZrAl (space group: Fd-3m) structures for various Al concentrations were constructed using the similar approach. We first randomly substituted 4% Cu atoms with Zr atoms, 100 times. Then we selected the $Cu_{46}Zr_{29}Al_{25}$ structure as the lowest energy minimized structure. Then Al atoms were substituted by Zr atoms to obtain the other Al concentrations.

For the CuZrAl crystal phase, we substituted 4.3% Zr atoms and 8.3% Al atoms with Cu atoms to build the crystal phase of $Cu_{46}Zr_{29}Al_{25}$. Then we constructed the low Al concentrations by substituting the Al atoms with Zr atoms.

We carried out NPT simulations on various crystal structures at ambient conditions for 100 ps and then heated the systems linearly to 800 K within 500 ps. The 2PT was then used to obtain the entropy and free energy from 20 ps of equilibrated NVT trajectories of the crystal phases at 800 K.

S3. Dynamical viscosity from MD approach

Viscosity is an important physical variable reflecting the dynamical response of materials under external stress. From a kinetic point of view, the shear viscosity plays an essential role in affecting the GFA since it determines rates for attaining the atomic arrangements required for crystal nucleation and growth. From linear response theory, the shear viscosity for shear in the xz plane can be extracted from the equation:

$$j_{xz}(p_z) = -\eta \times \dot{\gamma} \ , \qquad \text{(S1)}$$

where j_{xz} is the x component of the momentum flux along the z direction, $\dot{\gamma} = \partial v_x/\partial z$ is the velocity gradient or shear rate, and η is the shear viscosity coefficient or dynamical viscosity. For Newtonian materials, the dynamical viscosity is constant; however it is a function of shear rate for non-Newtonian materials.

To compute the dynamical viscosity from in atomic simulations, we can use either equilibrium MD or non-equilibrium molecular dynamics (NEMD) methods. The equilibrium approach uses the Green-Kubo integral to relate the viscosity to the fluctuations of off-diagonal terms of the stress tensor.

$$\eta = \frac{V}{3T}\int_0^{\infty}\langle\sum_{x<y} P_{xy}(t)P_{xy}(0)\rangle dt \qquad \text{(S2)}$$

Unfortunately this approach generally requires long simulation times (~ 100 ns), it is sensitive to the length of the time step, and it suffers from high thermal fluctuations that lead to a great deal of noise compare to final value.

The second approach is to use the SLLOD" algorithm[8] in NEMD to compute viscosity. In SLLOD, one imposes a uniform shear rate on the simulation box, and computes the shear stress as a function of time.

In this paper, we use a reverse-NEMD (R-NEMD) approach[9] in which an induced momentum flux is created by exchanging momenta between two particles in different regions of the simulation box to induce a shear velocity. Here we use the NVE ensemble to conserve the total momentum. To obtain the viscosity for the Newtonian limit, we extrapolate the viscosity calculated as a function of shear rate to obtain the zero-shear limit.

S4. Structure analysis with Voronoi tessellation

A number of approaches have been used to characterize liquid and amorphous structures. This includes radial distribution functions, Honeycutt-Andersen type analysis,[10] and Voronoi tessellation analysis.[11] In this paper we adopted the Voronoi tessellation analysis to examine the local atomic packing of the undercooled liquids as temperature approaches T_g. In the Voronoi analysis, the Voronoi polyhedron (VP) is constructed as the minimal polyhedron for a center atom obtained by bisecting the lines joining it to its nearest neighbors with the planar faces at right angles. The simulation box is then split into the atomic domains owned by each particle, similar to the Wigner-Seitz cell for crystalline materials. The VP shape can be characterized by a set of number (f3, f4, f5, f6, …), where fi is the number of i-edged polygons on the polyhedron.

SUPPLEMENTARY FIGURES

Figure S1

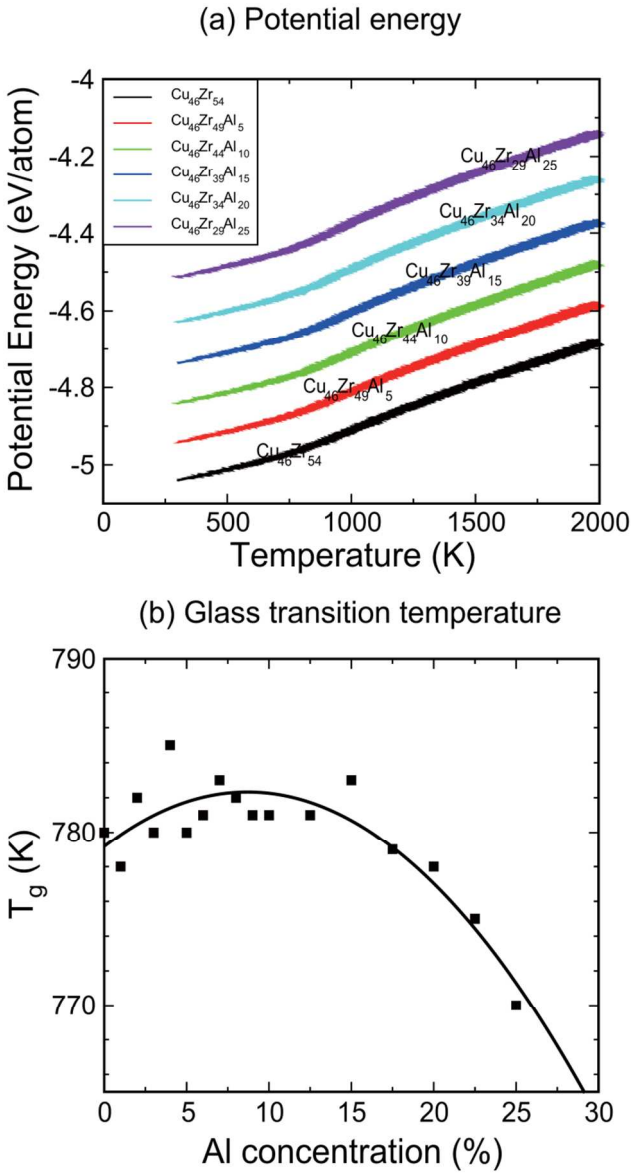

Figure S1. Thermodynamic properties of liquids and glass during quenching process for various Al concentrations. (a) Equation of state of liquid and glass under cooling. Increasing Al concentration increases the potential energy of the system. (b) T_g from the enthalpy fitting by Eq. (1) to various Al concentrations. The solid black line is the fiting results using the second order polynomial.

Figure S2

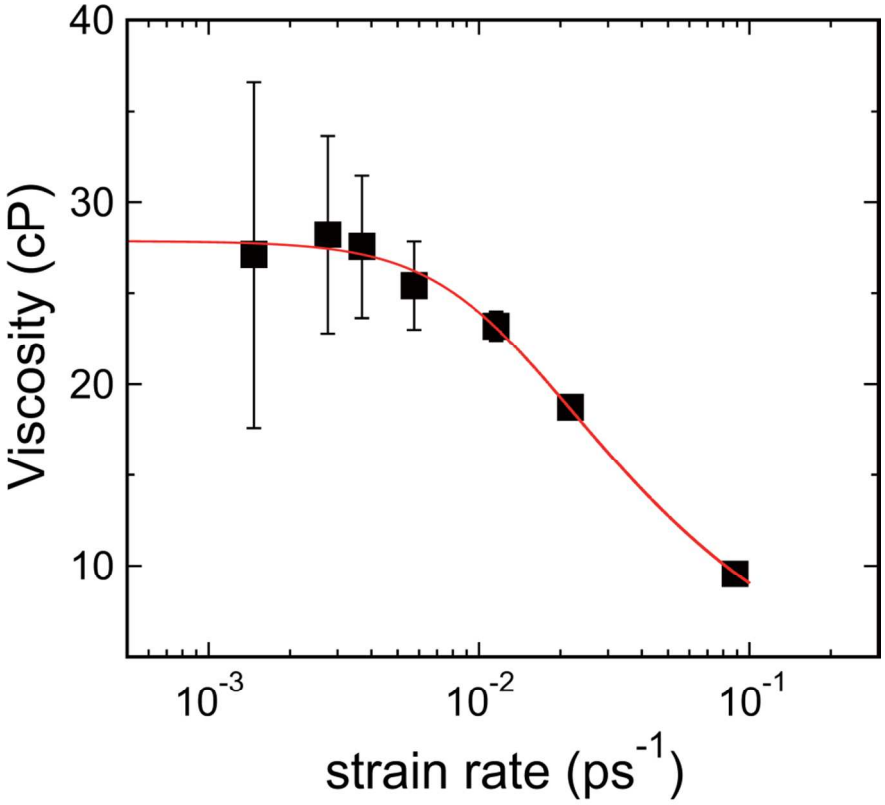

Figure S2. Dynamical viscosity as a function of strain rate for undercooled liquids $Cu_{46}Zr_{54}Al_{10}$ at T = 1000 K. The shear viscosity decreases with higher shear strain rates showing a shear-thinning behavior. The red line is fit with Curreau equation (Eq. 2) showing that the metallic liquid is a Newtonian fluid when shear strain rate is smaller than 0.5×10^{-3} per ps.

Figure S3

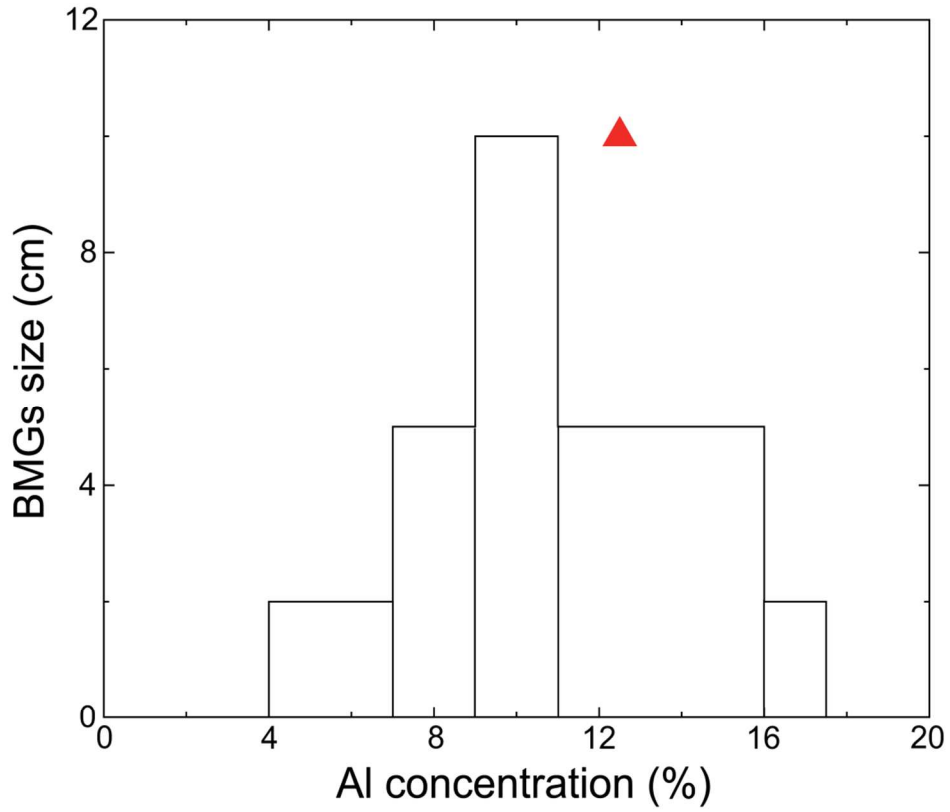

Figure S3: The comparison of GFA of experiment (lines) $Cu_{46}Zr_{54-x}Al_x$ (x varies from 0 to 20) with simulations (filled triangle). The experiment data are extracted from the contour map of ref. [12]. The filled red triangle is the best GFA regions from our simulation prediction (Just for comparison, we cannot get the BMGs sizes from the direct MD simulations). Based on our simulation model, the GFA will decreases when Al concentration decreases from 10 % to 0% or increases from 12.5 % to 25% which is exactly consistent with the experiment.

SUPPLEMENTARY TABLE

Table S1

Viscosity fitting parameters (VFT equation)

Al	T_0 (K)	D	η_0 (cP)
5%	480.4	2.99	1.00
10%	466.4	4.15	0.53
20%	443.5	4.16	0.60

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