



# The effect of enthalpy of mixing on the atomic level structure and plasticity of amorphous alloys: A molecular dynamics simulation study in a binary model system



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## ABSTRACT

Molecular dynamics simulations were performed to investigate the effect of the enthalpy of mixing on the atomic level structure and plasticity of binary metallic glasses by using an ideal model potential. Whereas some model alloys with a strong positive enthalpy of mixing solidified into mixtures of microcrystalline domains of face-centered cubic or hexagonal close-packed crystal structures, the other alloys solidified into amorphous structures. Various structural properties of the amorphous alloys were analyzed as a function of the enthalpy of mixing interaction parameter. The deformation behavior of the amorphous samples was discussed in terms of atomic-level structural features such as the fraction of icosahedral clusters, the degree of short-range ordering and potential energies of atomic clusters in order to find a clue on the relationship between the mechanical properties and atomic structure of the amorphous alloys.

## 1. Introduction

Metallic glasses are essentially frozen supercooled liquids and show exotic properties such as high strength, high elastic limit, good corrosion and wear resistance, and soft magnetic properties. Consequently, they have been considered as candidates for new structural and functional materials [1–5]. Due to a liquid-like long-range disordered structure and lack of dislocations, plastic deformation in metallic glasses is different from those in crystalline materials. For example, deformation in metallic glasses is usually localized in the nanoscale regions of shear bands, which leads to limited plastic flow and macroscopically brittle behavior. This could be one of the major issues that hinders engineering applications with metallic glasses [6–9].

The relationship between atomic structures and mechanical properties in metallic glasses has not yet been clearly understood due to the complexity of their disordered atomic structures compared to crystalline alloys [9–11]. Whereas the microstructures in crystalline alloys are well described in terms of phase, defects, and size distribution (all of which can be probed in detail with currently available techniques), the structure of metallic glasses cannot be described with a standardized form because the atoms in them are randomly distributed without long-range order.

Due to the difficulty in probing the atomic structure of metallic glasses, molecular dynamics simulations have been used to correlate their mechanical properties with their atomic structures [9]. Significant progress has been achieved in clarifying their atomic level structures and intrinsic deformation behavior, and according to previous molecular dynamics studies [9–19], the atomic structure of metallic glasses can be analytically described by combinations of various polyhedral packing units. Among them, icosahedral clusters (ICs) play a key role in the intrinsic plasticity of metallic glasses. Denoted by the Voronoi index  $\langle 0,0,12,0 \rangle$ , ICs possess high atomic packing density and are known to be mechanically and energetically more stable than other types of polyhedral packing units [12,20]. The fraction of and connectivity between ICs are reported to be correlated with the simulated plasticity of the metallic glasses in alloy systems [9,11–19].

For controlling the population of ICs in metallic glasses, the key property could be the average atomic size ratio between center atoms and their surrounding neighbors. This can be manipulated by several factors, such as the number of components, the atomic size ratio between the major constituent elements, and the enthalpy of mixing. These parameters are also well-known key factors in empirical rules [21–25] that are not only critical to the glass forming ability of alloys

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but also influential on the mechanical properties and deformation behavior of the fabricated metallic glasses. However, the effects of the enthalpy of mixing property on the deformation behavior of metallic glasses is not yet well understood.

In experimental studies of real metallic glass systems, it is difficult to see the effect of specific properties such as atomic size and enthalpy of mixing on plastic deformation behavior since many factors are operating simultaneously. Thus, the effect of a specific parameter cannot easily be separated from those of the other parameters. In this study, we focus on the effect of the enthalpy of mixing property on the glass forming ability, local atomic structure, and comprehensive plasticity of binary metallic glasses.

## 2. Computer simulations

### 2.1. Interatomic potential model for binary alloys

The interaction between elements *A* and *B* is described by Voter potential scheme in the framework of embedded-atomic method (EAM) models. The binary alloy potential model for the molecular dynamics simulations can be expressed as [26].

$$E = \sum_i \left[ F_{s_i}(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi_{s_i-s_j}(r_{ij}) \right], \quad (1)$$

where  $F_{s_i}(\rho)$  is the energy associated with embedding atoms of type  $s_i$  in a uniform electron gas of density  $\rho$  and  $\phi_{s_i-s_j}(r)$  is the pairwise interaction between atoms of type  $s_i$  and  $s_j$  separated by a distance  $r$ .

Within Voter's formalism [27], the electron density is given by

$$\bar{\rho}_i = \sum_{j(\neq i)} f(r_{ij}), \quad (2)$$

where the atomic electron density function  $f(r)$  is taken as the density of a hydrogenic 4s orbital:

$$f(r) = f_0 r^6 (e^{-\beta r} + 2^9 e^{-2\beta r}). \quad (3)$$

Here,  $\beta$  is an adjustable fitting parameter that quantifies the distance over which the electron density decays away from an atom position and  $f_0$  is a prefactor. Although the latter can be an arbitrary value for a unary system because it cancels out when combined with the embedding function, it is an adjustable parameter that should be determined for an alloy system.

The pair potential  $\phi(r)$  between atoms  $i$  and  $j$  takes the Morse potential form

$$\phi(r) = -D_M [2e^{-\alpha_M(r-R_M)} - e^{-2\alpha_M(r-R_M)}], \quad (4)$$

where  $D_M$ ,  $R_M$ , and  $\alpha_M$  are adjustable fitting parameters that define the well-depth of the Morse pair-interaction, the position of the minimum, and a measure of the curvature at the minimum, respectively.

As a final step, the embedding function  $F(\rho_i)$  is numerically determined so that the total energy of the reference system (here, it is set to be a face-centered cubic (fcc) crystal) as a function of dilation satisfies the following universal binding energy relationship: [26]

$$E(a) = -E_0 \left[ 1 + \alpha \left( \frac{a}{a_0} - 1 \right) \right] \exp \left[ -\alpha \left( \frac{a}{a_0} - 1 \right) \right], \quad (5)$$

where  $E_0$  is the cohesive energy,  $\alpha$  is the exponential decay factor for the universal energy function,  $a$  is the dilated lattice constant, and  $a_0$  is the equilibrium lattice constant.

Within the above formalism, we have seven adjustable parameters ( $\alpha$ ,  $\beta$ ,  $D_M$ ,  $r_M$ ,  $\alpha_M$ ,  $E_0$ , and  $a_0$ ) to be determined for a single-component potential. For a simpler potential model for idealized elements, we first assign a set of values for three of the parameters:  $\alpha = 5.0$ ,  $\beta = 4.0$ , and  $\alpha_M = 5.0$  so that the potential model can roughly present a typical range of properties for fcc metals. Secondly,  $D_M$  and  $r_M$  from the Morse pair interaction are related to the effective bond-dissociation energy  $\epsilon_0$

and the equilibrium interatomic distance  $r_0$ , respectively, as follows:  $D_M = 1/3\epsilon_0$ ,  $r_M = r_0$  (note that  $\epsilon_0$  is defined as having a positive value, thus the effective potential energy per bond is  $-\epsilon_0$ ). Likewise, the cohesive energy  $\epsilon_0$  and the equilibrium lattice constant  $a_0$  are set as  $E_0 = 6\epsilon_0$  and  $a_0 = \sqrt{2}r_0$ , respectively. Finally, for the model fcc metals, there remain only two adjustable parameters:  $\epsilon_0$  and  $r_0$ , which can be compared respectively to the equilibrium interatomic distance  $r(=\frac{1}{2}\bar{c})$  and potential well-depth  $\epsilon$  in Lennard-Jones models, and similarly respectively represent the effective bond energy between atoms and the equilibrium interatomic distance.

The potential interactions are smoothly cut-off at  $r = r_{cut}$  (usually between the third- and fourth-nearest-neighbor shells of a static fcc crystal) to ensure that the interatomic potential and its first derivatives are continuous.

Similar to the Lennard-Jones models, our model potential can be easily extended to binary or multicomponent alloy systems by using combinations of the two adjustable parameters:  $\epsilon_0$  and  $r_0$ . For instance, we can have three pairs of  $\epsilon_0$  and  $r_0$  for an *AB* binary alloy:  $(\epsilon_{A-A}, r_{A-A})$ ,  $(\epsilon_{B-B}, r_{B-B})$ , and  $(\epsilon_{A-B}, r_{A-B})$ . (As in the unary case,  $\alpha_M$  for pairwise interactions was fixed to 5.0 regardless of species).

For unary interactions,  $r_{s_i-s_j}$  and  $\epsilon_{s_i-s_j}$  ( $s_{ij} = A$  or  $B$ ) indicate a measure of atomic size and binding energy, respectively, and appropriate values can be independently assigned to the parameters  $r_{s_i-s_j}$  and  $\epsilon_{s_i-s_j}$  for either material *A* or material *B*. In this work, the equilibrium interatomic distance  $r_0$  and the effective bond-dissociation energy  $\epsilon_0$  were set as follows:  $r_A = 3.2 \text{ \AA}$ ,  $r_B = 2.56 \text{ \AA}$ , and  $\epsilon_{A-A} = \epsilon_{B-B} = 0.5 \text{ eV}$ . Note that the atomic size ratio  $r_{B/A}$  ( $= r_B/r_A$ ) was set to 0.8. On the other hand,  $\epsilon_{A-B}$  and  $r_{A-B}$  represent the effective bond-dissociation energy and interatomic distance, respectively, for the cross-species interaction and thereby can be a function of the combined properties of elements *A* and *B*. Here, for simplicity, we fixed  $r_{A-B}$  to be an arithmetic average of  $r_{A-A}$  and  $r_{B-B}$ , i.e.,  $r_{A-B} = (r_{A-A} + r_{B-B})/2 = 2.88 \text{ \AA}$ . However,  $\epsilon_{A-B}$  can be varied within a range of values depending on the relative bond strength between cross-species, i.e. enthalpy of mixing property of the alloy.

In order to represent a set of binary alloys with various values of enthalpy of mixing, a single dimensionless parameter  $\hat{\omega}$  was defined as follows:

$$\begin{aligned} \hat{\omega} &= - \left\{ \frac{\epsilon_{A-B} - \frac{1}{2}(\epsilon_{A-A} + \epsilon_{B-B})}{\frac{1}{2}(\epsilon_{A-A} + \epsilon_{B-B})} \right\} \\ &= - \left\{ \frac{\epsilon_{A-B}}{\frac{1}{2}(\epsilon_{A-A} + \epsilon_{B-B})} - 1 \right\}. \end{aligned} \quad (6)$$

As a normalized form,  $\hat{\omega}$ , called enthalpy of mixing interaction parameter, is similar to the one in quasi-chemical or regular solution models. For instance, if we consider a nearest-neighbor lattice model with fixed bond-dissociation energies  $\epsilon_{s_i-s_j}$  for  $s_i - s_j$  pair types (like regular solution models), the enthalpy of mixing for random solid solutions will be  $\Delta H_{mix} \simeq \hat{\omega} \epsilon_0 \bar{z} X_A X_B$ , where  $\bar{z}$  and  $X_j$  are the number of bonds per atom (coordination number (CN)) and the mole fraction, respectively. Note that since we fixed  $\epsilon_{A-A} = \epsilon_{B-B} = 0.5 \text{ eV}$ ,  $\hat{\omega}$  is an explicit function of  $\epsilon_{A-B}$ , i.e.,  $\hat{\omega}(\epsilon_{A-B}) = -(\epsilon_{A-B} - 0.5)/0.5$  and vice versa ( $\epsilon_{A-B}(\hat{\omega}) = 0.5(1 - \hat{\omega}) \text{ eV}$ ).

The more negative the value of  $\hat{\omega}$ , the stronger the negative enthalpy of mixing of the alloy system. However, unlike in quasi-chemical models of fixed lattice and constant bond energy, enthalpies of mixing  $\Delta H_{mix}$  of general binary alloys in molecular dynamics simulations are dependent on the actual atomic configuration in complicated ways. In fact, the enthalpy of mixing  $\Delta H_{mix}$  is determined by combination of parameters such as  $r_{s_i-s_j}$ ,  $\epsilon_{s_i-s_j}$ , and the composition. In the case of a large atomic size mismatch,  $\Delta H_{mix}$  is substantially positive when  $\hat{\omega} = 0$ . Nevertheless, the interaction parameter  $\hat{\omega}$  is a good measure of enthalpy of mixing for binary alloys and plays as a key factor in our simulation study. In this work, we varied  $\hat{\omega}$  from  $-20\%$  to  $+10\%$  to investigate the effect of the enthalpy of mixing on the atomic level structure and

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