

Incorporation of defects into the central atoms model of a metallic glass

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Abstract

The central atoms model (CAM) of a metallic glass is extended to incorporate thermodynamically stable defects, similar to vacancies in a crystalline solid, within the amorphous structure. A bond deficiency (BD), which is the proposed defect present in all metallic glasses, is introduced into the CAM equations. Like vacancies in a crystalline solid, BDs are thermodynamically stable entities because of the increase in entropy associated with their creation, and there is an equilibrium concentration present in the glassy phase. When applied to Cu–Zr and Ni–Zr binary metallic glasses, the concentration of thermally induced BDs surrounding Zr atoms reaches a relatively constant value at the glass transition temperature, regardless of composition within a given glass system. Using this “critical” defect concentration, the predicted temperatures at which the glass transition is expected to occur are in good agreement with the experimentally determined glass transition temperatures for both alloy systems.

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1. Introduction

The central atoms model (CAM) was first developed in the 1960s as an extension of the quasicchemical model [1–4]. It has been used primarily to study the thermodynamics of crystalline phases, particularly interstitial solid solutions in steels. In a recent paper by the present authors, CAM was adapted to describe the atomic structure of a binary metallic glass [5]. In the treatment, the local atomic short-range order (SRO) inherent in glassy metals was used to describe the system in terms of a “central” atom and a cage of nearest neighbors (NNs) surrounding it. The equations were modified to account for the lack of long-range order (LRO) associated with the glassy state. Topological SRO (TSRO) was accounted for by considering the local atomic packing around each central atom. The relative atomic sizes of the species were used to describe NN cages that

most efficiently occupy the space surrounding a central atom. These NN configurations form “geometrically preferred” arrangements because they minimize the average atomic volume [7–11], and were termed “ideal” NN cages. Chemical SRO (CSRO) was introduced by calculating the energy per atom associated with each NN cage using atomic interaction energies extracted from thermodynamic data.

Because of the disordered nature of a metallic glass, deviations from ideal TSRO and CSRO are likely to occur. The authors have referred to these deviations as bond-deficiencies (BDs) [12–14]. These BD defects are akin to vacancies in a crystalline material, and contribute to “extra” volume of the amorphous phase often described using the free volume (FV) model. Just as for vacancies, entropy effects will result in a non-zero concentration of point defects in thermodynamic equilibrium at a finite temperature. Unlike a vacancy, which is defined as the absence of an atom on a lattice site, a BD is described as a NN cage containing one fewer atom than an ideal cage.

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Nomenclature

$C_{Z_j^i}; C_{Z_j^i-1}$	combinatorial factor enumerating the number of different arrangements of i B and $Z_j^i - i$ A atoms ($C_{Z_j^i}$); and for i B and $Z_j^i - 1 - i$ A atoms ($C_{Z_j^i-1}$)	$X_J^i; X_J^{m'}$	effective mole fraction of species J in the system, accounting for differences in average coordination number between species; m indicates for BD NN cages
E	molar internal energy of the system	$X_{J,K}^i$	mole fraction of species K in a NN cage containing i B and $Z_j^i - i$ A atoms around a J central atom; i.e., $X_{J,B}^i = i/Z_j^i$ and $X_{J,A}^i = (Z_j^i - i)/Z_j^i$
$f_A; f_A^m$	ratio of average coordination numbers of A to B atoms, used to calculate “effective” compositions in the amorphous phase; m indicates the ratio for BD NN cages	z_{JK}	partial coordination number of K atoms surrounding a J central atom
F	molar Helmholtz free energy of the system	Z_j^i	total coordination number of a NN cage containing i B atoms and $Z_j^i - i$ A atoms around a J central atom
$g; g^*$	degeneracy factor: the number of possible configurations a system may undertake; $*$ indicates the case of random mixing	$Z_j^{\max}$	maximum number of B atoms that can fit in a NN cage surrounding a J central atom
G	molar Gibbs free energy of the system	Z_j^K	coordination number calculated for a J solute atom surrounded completely by solvent atoms of species K , calculated from the ECP model
h	correction factor required in the calculation of g	α	constant used in estimating the energy of structural relaxation
i	the number of B atoms in a NN cage	δ_j^i	fractional deviation of the unoccupied space in a NN cage from that found in ideal dense random packing or 0.025
k	Boltzmann’s constant	ε_j^i	NN cage energy prior to structural relaxation; or the average cohesive energy per atom
$m; m^e$	fraction of atoms surrounded by a BD NN cage; superscript e indicates the equilibrium fraction	$\varepsilon_j^i; \varepsilon_j^{im}$	energy of a NN cage containing i B and $Z_j^i - i$ A atoms around a J central atom for ε_j^i ; and of a BD NN cage containing i B and $Z_j^i - 1 - i$ A atoms for ε_j^{im}
$m_J; m_J^e$	fraction of atoms of species J surrounded by a BD NN cage; superscript e indicates the equilibrium fraction	ε_{SR}	energy of structural relaxation
N	total number of atoms (or atoms plus vacancies in a crystalline material) in a system	λ_n	Lagrange multiplier associated with the constraint Ψ_n ; no subscript indicates the Lagrange multiplier associated with a mass balance constraint (Ψ_3) in Eq. (16)
N_J	number of atoms of species J in a system; subscript V stands for vacancies	$\Lambda_6; \Lambda_7$	ratios related to λ_4 and λ_5 , equal to $\Lambda_6 = 1/\Lambda_7 = e^{-\lambda_5}/e^{-\lambda_4}$
N_a	Avogadro’s number	Ψ_n	constraint imposed on the NN cage probabilities p_j^i and p_j^{i*} ; no subscript indicates the Lagrange multiplier associated with a mass balance constraint (Ψ_3) in Eq. (6)
$p_j^i; p_j^{i*}$	probability of finding an ideal NN cage with i B and $Z_j^i - i$ A atoms around a J central atom, equal to $C_{Z_j^i} \cdot \alpha_j^i$ (or $C_{Z_j^i} \cdot \alpha_j^{i*}$); $*$ indicates random mixing		
$p_j^{im}; p_j^{im*}$	probability of finding a BD NN cage with i B and $Z_j^i - 1 - i$ A atoms around a J central atom, equal to $C_{Z_j^i-1} \cdot \alpha_j^{im}$ (or $C_{Z_j^i-1} \cdot \alpha_j^{im*}$); $*$ indicates random mixing		
P_j^i	total packing efficiency of a NN cage containing i B atoms around a J central atom		
P_{JK}	partial packing efficiency of K atoms around a J atom, given by $P_{JK} = z_{JK}/Z_j^K$		
S	molar entropy of the system		
X_J	mole fraction of species J in the system		

This definition, and the lack of well-defined lattice positions in a glassy metal, allows the remaining atoms in a NN cage to be redistributed within the cage, minimizing the cost of BD formation in terms of energy and volume. In a previous treatment of metallic glasses using CAM, these BD defects were neglected for simplicity in the previous treatment. The present effort incorporates them into CAM, creating a more realistic description of the glassy structure, which may then be utilized to describe not only selected structural and thermodynamic properties, but

extra volume associated with the amorphous phase and kinetic behavior as well.

2. Formulation

2.1. “Ideal” metallic glass

The complete derivation of the equations of CAM can be found elsewhere [1–6]. From the derivation, assuming enthalpy and internal energy are equal, the molar Gibbs

free energy of an “ideal” binary metallic glass (i.e., one containing no defects) is expressed using CAM as:

$$G = N_A X_A \sum_{i=0}^{Z_A^{\max}} p_A^i c_A^i + N_B X_B \sum_{i=0}^{Z_B^{\max}} p_B^i c_B^i + N_A kT \left[(X_A \ln X_A + X_B \ln X_B) + \sum_{i=0}^{Z_A^{\max}} X_A p_A^i \ln \left(\frac{X_A p_A^i}{C_{Z_A^i}} \right) + \sum_{i=0}^{Z_B^{\max}} X_B p_B^i \ln \left(\frac{X_B p_B^i}{C_{Z_B^i}} \right) - \sum_{i=0}^{Z_A^{\max}} X_A p_A^{i*} \ln \left(\frac{X_A p_A^{i*}}{C_{Z_A^i}} \right) - \sum_{i=0}^{Z_B^{\max}} X_B p_B^{i*} \ln \left(\frac{X_B p_B^{i*}}{C_{Z_B^i}} \right) \right] \quad (1)$$

where C_{Z_j} is the combinatorial factor:

$$C_{Z_j} = \frac{Z_j!}{(Z_j - i)! i!} \quad (2)$$

enumerating the number of different arrangements of i B atoms and $Z_j - i$ A atoms. p_j^* and p_j^i are the probabilities of finding a J central atom surrounded by a NN cage consisting of i B atoms and $Z_j - i$ A atoms, for the case of random mixing of the atoms (p_j^*), and for ordering (or segregation) of the atoms due to the thermodynamic interaction between the species (p_j^i). These probabilities are given by the equations:

$$p_j^* = \frac{C_{Z_j} (X'_A)^{Z_j-i} (X'_B)^i}{\sum_{i=0}^{Z_j^{\max}} C_{Z_j} (X'_A)^{Z_j-i} (X'_B)^i} \quad (3)$$

and

$$p_j^i = \frac{C_{Z_j} \exp \left[- \left(\frac{e_j^i}{kT} + i\lambda \right) \right]}{\sum_{i=0}^{Z_j^{\max}} C_{Z_j} \exp \left[- \left(\frac{e_j^i}{kT} + i\lambda \right) \right]} \quad (4)$$

The effective composition variables, X'_j , in Eq. (3), account for the differences in the average coordination number between the two species that arise due to differences in atomic size and the lack of LRO in a metallic glass, and are defined as:

$$X'_A \equiv \frac{f_A X_A}{f_A X_A + X_B} \quad \text{and} \quad X'_B \equiv \frac{X_B}{f_A X_A + X_B}. \quad (5)$$

Both f_A and λ in Eq. (4) are determined by applying a mass balance constraint, Ψ , on p_j^* and p_j^i

$$\Psi = X_A \sum_{i=0}^{Z_A^{\max}} i p_A^i + X_B \sum_{i=0}^{Z_B^{\max}} i p_B^i - X_B \sum_{i=0}^{Z_B^{\max}} Z_B^i p_B^i = 0. \quad (6)$$

This restricts the number of B atoms found in both A and B atom NN cages to be equal to the total number of B atom NNs.

2.2. Metallic glass containing defects

2.2.1. Bond deficiencies

The above equations provide the necessary tools for describing a defect-free amorphous phase using CAM.

Once the possible types of NN cages that can occur, and their associated enthalpies, are determined for a given system, the thermodynamic stability and CSRO of the glass can then be studied [5,6]. However, the simplification made above is that only ideal-type NN cages occur within the glassy structure. Although a useful approximation, actual metallic glasses contain many topological defects due to their disordered nature, disrupting these ideal NN configurations. The inclusion of defects in a thermodynamic model of a metallic glass is therefore essential. Vacancy-like defects, akin to those found in crystalline materials, are not appropriate in describing point defects in a metallic glass because the cost of formation, in terms of energy and volume, is too large to be consistent with experimental observation [15]. A BD, introduced by Zhu et al. [12–14], is a more suitable method of describing the nature of defects in a metallic glass. Fig. 1 illustrates the idea of a BD for a 2-D NN cage. The light-colored atom switches from a first NN to a second NN position from Fig. 1a and b, creating a bond-deficient NN cage around the central atom.

Like vacancies in a crystalline solid, BDs are thermodynamically stable because of the increase in entropy associated with their formation. Thus, there will be an equilibrium concentration of BDs present in the amorphous structure at temperatures above absolute zero.

In a crystal, a vacancy is essentially the absence of an atom on a lattice site, and thus the formation energy and volume required for its creation is of the order of the cohesive energy per atom and average atomic volume, respectively. However, for the case of a thermally induced BD, instead of breaking the entire complement of bonds corresponding to the removal of one atom, only one bond is broken with the central atom (one atom is missing from ideal SRO), and the remaining NNs are redistributed. This significantly reduces the energy cost of defect creation, which can be as low as $1/(2Z_j^i)$ that of a vacancy [12]. The volume cost of creating a BD is also only a fraction ($\sim 1/5$) that of a vacancy. A double BD (similar to a double vacancy) is also a possible configuration. However, the probability of their occurrence is quite small, and only atoms having a single BD in their NN cage are considered

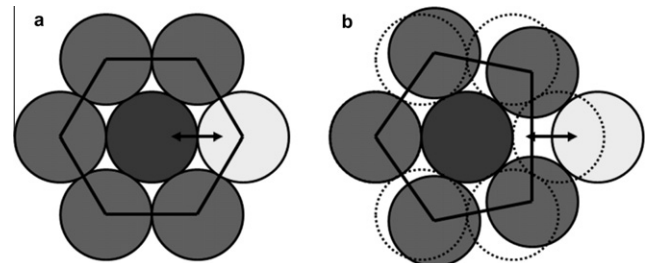


Fig. 1. A 2-D schematic representation of a bond deficiency in a metallic glass. (a) A perfect NN cage surrounding the central atom corresponding to ideal hexagonal packing. (b) A thermodynamically necessary BD formed when the light-colored atom switches from a first NN to a second NN position. The resulting NN cage around the central atom is bond deficient, i.e., one fewer bond than ideal packing.

in the present development. Like vacancies, BDs are thermodynamically stable, and there is a finite concentration present in a metastable equilibrium glassy structure. These structural defects are considered to provide the primary vehicle for atomic transport responsible for diffusion, glass transition and, to some extent, plastic flow [12–14].

2.2.2. Including BDs in CAM

To incorporate a BD in the CAM description, the equations must be derived in such a way that defects are included. Consider the free energy of a system in terms of the internal energy, E , and the number of possible configurations having that energy, g , given as [1–4]:

$$G \approx F = E - N_a kT \ln(g). \quad (7)$$

For random mixing in a simple binary crystalline system, disregarding defects, g is equal to $N!/(N_A!N_B!)$. If vacancies are included in the description of g for a crystalline phase, they occupy lattice sites, and thus act as a third species. Therefore, g becomes:

$$g^* = \frac{N!}{N_A!N_B!N_V!}. \quad (8)$$

The asterisk is added to denote a random mixing process. Unlike vacancies, BDs do not occupy lattice sites (or pseudo-lattice sites for the case of a glass). Thus, for a metallic glass, they can be freely distributed and associated with any of the atoms in the system. For random mixing, the total number of possible configurations the system may exhibit is equal to the total number of ways of arranging the atoms, multiplied by the number of ways of arranging some concentration, m , of BD NN cages, around the atoms. Thus, g^* becomes:

$$\begin{aligned} g^* &= (\text{\#ways of arranging atoms}) \\ &\quad \times (\text{\#ways of arranging BDs}) \\ &= \frac{N!}{N_A!N_B!} \times \frac{N!}{(mN)![(1-m)N]!} \\ &= \frac{(N!)^2}{N_A!N_B!(mN)![(1-m)N]!} \end{aligned} \quad (9)$$

where N is now the total number of atoms, i.e., pseudo-lattice sites, or $N_A + N_B$. In this randomly mixed solution, any particular central atom, J , may be surrounded by an ideal NN cage containing Z_J^i atoms, or a BD NN cage having $Z_J^i - 1$ NNs. The probability of each of these configurations occurring is:

$$p_J^{i*} = (1-m)C_{Z_J^i-1} \alpha_J^{i*} \quad (10)$$

for ideal NN cages, and:

$$p_J^{im*} = mC_{Z_J^i-1} \alpha_J^{im*} \quad (11)$$

for BD NN cages, with

$$\alpha_J^{i*} = \frac{(X_A')^{Z_J^i-1} (X_B')^i}{\sum_{i=0}^{Z_J^{\max}} C_{Z_J^i-1} (X_A')^{Z_J^i-1} (X_B')^i} \quad (12)$$

and

$$\alpha_J^{im*} = \frac{(X_A^{m'})^{Z_J^i-1-i} (X_B^{m'})^i}{\sum_{i=0}^{Z_J^{\max}-1} C_{Z_J^i-1} (X_A^{m'})^{Z_J^i-1-i} (X_B^{m'})^i} \quad (13)$$

$X_J^{m'}$ is the effective composition of species J in BD NN cages, described similarly to Eq. (5), except now considering the coordination number of BD cages ($Z_J^i - 1$). Similarly, $C_{Z_J^i-1}$ is of the same form as Eq. (2), or the number of different possible atomic arrangements for each value of i in BD NN cages.

If the atoms are not distributed randomly, and instead segregation or ordering occurs, the description of g is different than Eq. (9). For this case, if the N_A A atom NN cages and N_B B atom NN cages, both containing some partial fraction of cages containing a BD, m_A and m_B , respectively, are distributed independently of one another, g is expressed as:

$$g = h \frac{N_A!N_B!}{\prod_{i=0}^{Z_A^{\max}} [(N_A \alpha_A^i)!]^{C_{Z_A^i-1}} \prod_{i=0}^{Z_A^{\max}-1} [(N_A \alpha_A^{im})!]^{C_{Z_A^i-1}} \prod_{i=0}^{Z_B^{\max}} [(N_B \alpha_B^i)!]^{C_{Z_B^i-1}} \prod_{i=0}^{Z_B^{\max}-1} [(N_B \alpha_B^{im})!]^{C_{Z_B^i-1}}} \quad (14)$$

where α_J^i and α_J^{im} are now the probability of a J atom surrounded by i B atoms and $Z_J^i - i$ or $Z_J^i - i - 1$ A atoms for ideal and BD cages, respectively. The numerator of Eq. (14) exhibits the total number of NN cages, while the denominator accounts for the different types of cages. A correction factor, h , is added because all NN cages cannot, in reality, be distributed independently of one another (each NN atom is a central atom of another NN cage). If the α_J^i and α_J^{im} in Eq. (14) are replaced by their values for a random mixing process, α_J^{i*} and α_J^{im*} , respectively, and the result is equated to Eq. (9), the appropriate value of h is determined. In this manner, g for a defect-containing metallic glass can be determined, and the expression for the Gibbs free energy is given by:

$$\begin{aligned} G &= N_a \left[X_A \left(\sum_{i=0}^{Z_A^{\max}} p_A^i \epsilon_A^i + \sum_{i=0}^{Z_A^{\max}-1} p_A^{im} \epsilon_A^{im} \right) + X_B \left(\sum_{i=0}^{Z_B^{\max}} p_B^i \epsilon_B^i + \sum_{i=0}^{Z_B^{\max}-1} p_B^{im} \epsilon_B^{im} \right) \right] \\ &\quad + N_a kT [X_A \ln X_A + X_B \ln X_B + m \ln m + (1-m) \ln (1-m)] \\ &\quad + N_a kT \left[X_A \sum_{i=0}^{Z_A^{\max}} p_A^i \ln \left(\frac{X_A p_A^i}{C_{Z_A^i-1}} \right) + X_B \sum_{i=0}^{Z_B^{\max}} p_B^i \ln \left(\frac{X_B p_B^i}{C_{Z_B^i-1}} \right) \right. \\ &\quad \left. + \sum_{i=0}^{Z_A^{\max}-1} X_A p_A^{im} \ln \left(\frac{X_A p_A^{im}}{C_{Z_A^i-1}} \right) + \sum_{i=0}^{Z_B^{\max}-1} X_B p_B^{im} \ln \left(\frac{X_B p_B^{im}}{C_{Z_B^i-1}} \right) \right. \\ &\quad \left. - \sum_{i=0}^{Z_A^{\max}} X_A p_A^{i*} \ln \left(\frac{X_A p_A^{i*}}{C_{Z_A^i-1}} \right) - \sum_{i=0}^{Z_B^{\max}} X_B p_B^{i*} \ln \left(\frac{X_B p_B^{i*}}{C_{Z_B^i-1}} \right) \right. \\ &\quad \left. - \sum_{i=0}^{Z_A^{\max}-1} X_A p_A^{im*} \ln \left(\frac{X_A p_A^{im*}}{C_{Z_A^i-1}} \right) - \sum_{i=0}^{Z_B^{\max}-1} X_B p_B^{im*} \ln \left(\frac{X_B p_B^{im*}}{C_{Z_B^i-1}} \right) \right] \end{aligned} \quad (15)$$

The p_J^i and p_J^{im} are determined by first imposing five constraints on the probabilities, given by the equations:

$$\Psi_1 = \sum_{i=0}^{Z_A^{\max}} p_A^i + \sum_{i=0}^{Z_A^{\max}-1} p_A^{im} - 1 = 0$$

$$\Psi_2 = \sum_{i=0}^{Z_B^{\max}} p_B^i + \sum_{i=0}^{Z_B^{\max}-1} p_B^{im} - 1 = 0$$

$$\begin{aligned}
\Psi_3 &= X_A \left[\sum_{i=0}^{Z_A^{\max}} i p_A^i + \sum_{i=0}^{Z_A^{\max}-1} i p_A^{im} \right] + X_B \left[\sum_{i=0}^{Z_B^{\max}} i p_B^i + \sum_{i=0}^{Z_B^{\max}-1} i p_B^{im} \right] \\
&\quad - X_B \left[\sum_{i=0}^{Z_B^{\max}} Z_B^i p_B^i + \sum_{i=0}^{Z_B^{\max}-1} (Z_B^i - 1) p_B^{im} \right] = 0 \\
\Psi_4 &= X_A \sum_{i=0}^{Z_A^{\max}} p_A^i + X_B \sum_{i=0}^{Z_B^{\max}} p_B^i - (1 - m) = 0 \\
\Psi_5 &= X_A \sum_{i=0}^{Z_A^{\max}-1} p_A^{im} + X_B \sum_{i=0}^{Z_B^{\max}-1} p_B^{im} - m = 0
\end{aligned} \quad (16)$$

Ψ_1 and Ψ_2 confine the NN cage probabilities around each species to equal 1, Ψ_3 is a mass or bond balance of B atoms, and Ψ_4 and Ψ_5 arise because the total concentration of ideal cages and BD cages must be equal to $1 - m$ and m , respectively. Utilizing the method of Lagrange multipliers, and minimizing the free energy in Eq. (15) with respect to the p_j^i and p_j^{im} , the expressions for the NN cage probabilities are derived to be:

$$\begin{aligned}
p_A^i &= \frac{C_{Z_A^i} \exp \left[-\left(\frac{d_A^i}{kT} + i\lambda \right) \right]}{\sum_{i=0}^{Z_A^{\max}} C_{Z_A^i} \exp \left[-\left(\frac{d_A^i}{kT} + i\lambda \right) \right] + A_6 \sum_{i=0}^{Z_A^{\max}-1} C_{Z_A^i-1} \exp \left[-\left(\frac{d_A^{im}}{kT} + i\lambda \right) \right]} \\
p_B^i &= \frac{C_{Z_B^i} \exp \left[-\left(\frac{d_B^i}{kT} + i\lambda \right) \right]}{\sum_{i=0}^{Z_B^{\max}} C_{Z_B^i} \exp \left[-\left(\frac{d_B^i}{kT} + i\lambda \right) \right] + A_6 e^{-\lambda} \sum_{i=0}^{Z_B^{\max}-1} C_{Z_B^i-1} \exp \left[-\left(\frac{d_B^{im}}{kT} + i\lambda \right) \right]} \\
p_A^{im} &= \frac{C_{Z_A^i-1} \exp \left[-\left(\frac{d_A^{im}}{kT} + i\lambda \right) \right]}{A_7 \sum_{i=0}^{Z_A^{\max}} C_{Z_A^i} \exp \left[-\left(\frac{d_A^i}{kT} + i\lambda \right) \right] + \sum_{i=0}^{Z_A^{\max}-1} C_{Z_A^i-1} \exp \left[-\left(\frac{d_A^{im}}{kT} + i\lambda \right) \right]} \\
p_B^{im} &= \frac{e^{-\lambda} C_{Z_B^i-1} \exp \left[-\left(\frac{d_B^{im}}{kT} + i\lambda \right) \right]}{A_7 \sum_{i=0}^{Z_B^{\max}} C_{Z_B^i} \exp \left[-\left(\frac{d_B^i}{kT} + i\lambda \right) \right] + e^{-\lambda} \sum_{i=0}^{Z_B^{\max}-1} C_{Z_B^i-1} \exp \left[-\left(\frac{d_B^{im}}{kT} + i\lambda \right) \right]}
\end{aligned} \quad (17)$$

where λ_4 and λ_5 (the Lagrange multipliers for Ψ_4 or Ψ_5 , respectively) have been combined into the two ratios A_6 and A_7 , such that:

$$A_6 = \frac{1}{A_7} = \frac{e^{-\lambda_5}}{e^{-\lambda_4}} \quad (18)$$

A_6 and A_7 are determined by inserting the p_j^i and p_j^{im} into Ψ_4 or Ψ_5 and expanding the constraint into a quadratic equation. The resulting quadratic equation for Ψ_4 is

$$\begin{aligned}
&[(1 - m)\sigma_A^m \sigma_B^m] A_6^2 + [(X_A - m)\sigma_A^m \sigma_B + (X_B \\
&\quad - m)\sigma_A \sigma_B^m] A_6 - m\sigma_A \sigma_B \\
&= 0,
\end{aligned} \quad (19)$$

where σ_j and σ_j^m are the sums of the numerator of each p_j^i and p_j^{im} in Eqs. (17), from $i = 0$ to $Z_j^{\max}$ ($Z_j^{\max} - 1$ for BD NN cages).

The above equations allow for the thermodynamics and atomic structure of a metallic glass containing defects to be described using CAM. Because BDs are thermodynamically stable, an equilibrium concentration, m^e , can be calculated for a given temperature and composition by minimizing the free energy expression of Eq. (15). This equilibrium defect concentration can then be used to gain some information on the kinetics of the system.

2.3. NN cages and enthalpies

2.3.1. Possible NN cages

How Z_j^i varies with i for ideal NN cages depends on the relative sizes of the atoms and how they most efficiently fill the space surrounding the central atom. These ideal NN cage units can be described in a number of ways, such as considering of the solid angle occupied by NN atoms, as suggested by Egami [7,8]; or using the more recent efficient cluster packing (ECP) model of Miracle [9–11]. For solute of atoms species J , completely surrounded by solvent atoms of species K , the ECP model yields a coordination number given by [11]:

$$Z_J^K = \begin{cases} \frac{4\pi}{6\cos^{-1}\{\sin(\pi/3)\sqrt{1-[r_K/(r_J+r_K)]^2}\}-\pi} & \text{for } 0.225 \leq \frac{r_J}{r_K} \leq 0.414 \\ \frac{4\pi}{8\cos^{-1}\{\sin(\pi/4)\sqrt{1-[r_K/(r_J+r_K)]^2}\}-2\pi} & \text{for } 0.414 \leq \frac{r_J}{r_K} \leq 0.902 \\ \frac{4\pi}{10\cos^{-1}\{\sin(\pi/5)\sqrt{1-[r_K/(r_J+r_K)]^2}\}-3\pi} & \text{for } \frac{r_J}{r_K} \geq 0.902 \end{cases} \quad (20)$$

Eq. (20) maximizes the packing efficiency for a given radius ratio r_J/r_K . When a NN cage contains more than one type of atom, a partial packing efficiency for each species, $P_{JK} = z_{JK}/Z_J^K$, is defined. The sum of the partial packing efficiencies is constrained to not exceed unity. Considering a binary A – B system, for a given value of i (number of B NNs), the total packing efficiency, P_A^i , must satisfy the inequality:

$$\frac{i}{Z_B^A} + \frac{Z_A^i - i}{Z_A^A} \leq 1 \quad (21)$$

and similarly for B atom NN cages. Z_j^i is calculated by determining the maximum number of A atoms, $Z_j^i - i$, for each possible number of B atoms in the NN cage, i . The coordination numbers calculated in this manner correspond to the most efficiently packed NN configurations possible for a given value of i . The difference between the geometrical ECP model and CAM is that in the present model, all possible clusters satisfying Eq. (21) can be considered as possible NN arrangements, not only the most efficiently packed ones. Thermodynamic interactions between species are used to determine which configurations occur most often, or the CSRO.

The BD NN cages that may occur are assumed to be identical to those calculated using Eq. (21), except they contain $Z_j^i - 1 - i$ A atoms instead of $Z_j^i - i$. Thus, each BD NN cage contains one fewer A atom than an ideal configuration. Table 1 shows the possible ideal and BD NN cage configurations for Cu and Zr central atoms in the Cu–Zr binary system. Atomic radii of 0.128 and 0.159 nm are used for Cu and Zr, respectively. As an example, for values of i from 5 to 7, Z_{Cu}^i has a value of 11. With a BD, this results in NN cages containing 10 atoms. The possible BD cage configurations with 10 total NNs are 5 Cu and 5 Zr atoms, 4 Cu and 6 Zr atoms, and 3 Cu and 7 Zr atoms. Additional arrangements containing 6 Cu atoms

Table 1

Total coordination numbers for ideal NN cages (columns 1 and 4) and NN cages containing one BD (columns 2 and 5) as a function of i , the number of Zr atoms in the NN cage, for Cu and Zr central atoms in the Cu–Zr system.

Z_{Cu}^i	$Z_{\text{Cu}}^i - 1$	i (# Zr atoms)	Z_{Zr}^i	$Z_{\text{Zr}}^i - 1$
13	12	0	16	15
13	12	1	16	15
12	11	2	16	15
12	11	3	16	15
12	11	4	15	14
11	10	5	15	14
11	10	6	15	14
11	10	7	15	14
10	9	8	14	13
10	9	9	14	13
10	NA	10	14	13
		11	13	12
		12	13	12
		13	13	NA

and 4 Zr atom, 7 Cu atoms and 3 Zr atom, or 8 Cu and 2 Zr atoms are also possible configurations containing 10 total NNs; however, these are double BD configurations, i.e., $i = 2, 3$ and 4 Zr atoms with two fewer Cu atoms than the ideal Z_{Cu}^i instead of only one, and are not considered in the present treatment.

2.3.2. NN cage enthalpy and structural relaxation

The enthalpy of each NN cage is calculated by summing the energies of all the bonds that the central atom makes with its NNs. Atomic-level interaction energies have been extracted from CALPHAD-type thermodynamic data using a technique previously developed by the present authors [16]. Because the CALPHAD assessments are optimized to best fit experimental data, the atomic interaction parameters calculated using this method are consistent with other calculations and experimental observation. Three-body interactions, described elsewhere, are used in the present work because of their advantages when the model is extended to a ternary system [5,6,16]. The thermodynamic data for the Cu–Zr and Ni–Zr binary systems used in the following calculations can be found elsewhere [5].

As Z_j^i varies with i , jumps in energy occur when Z_j^i changes because fewer (or more) atoms can fit around the central atom. In a real system, these energy jumps are lessened by the redistribution of the surrounding atoms to more uniformly occupy volume, often termed structural relaxation. This is analogous to the idea of “ghost” bonding in vacancy formation [17]. A rigorous treatment of the energy associated with atomic relaxation requires detailed calculations of local electron densities and atomic-level stresses. A simple approximation can be made by assuming that, for small deviations in packing efficiency, the energy associated with this process, ε_{SR} , is linearly proportional to the amount of unoccupied space around the central atom. For the case where $r_A/r_B = 1$ (pure-component packing), Eq. (20) yields a value of $Z_j^K = 13.33$, implying that 13

atoms of identical size can fit in a NN cage surrounding a central atom. This results in a total packing efficiency of 13/13.33, or 0.975; and a fraction of unoccupied space is 1–0.975 or 0.025. In the following calculations, ε_{SR} is estimated as $-\alpha \cdot \delta_j^i \cdot \varepsilon_j^i$, where δ_j^i is the fractional difference between the unoccupied space in the NN cage and the ideal value of 0.025. The parameter α is an adjustable parameter. It is assigned a value such that ε_{SR} where δ_j^i is largest (where Z_j^i changes) is $\sim \varepsilon_j^i / (3Z_j^i)$. This is also the approximate energy of a ghost bond in a crystalline material [12,17]. For the Cu–Zr and Ni–Zr systems under consideration here, a value of $\alpha = 0.3$ yields a reasonable estimate of ε_{SR} . Fig. 1a illustrates the energy per atom for ideal Cu-atom NN cages in the Cu–Zr system before and after adding the estimated energy of structural relaxation.

The above approximation is a good estimate of ε_{SR} as long as the deviation from ideal packing efficiency is small (a linear relationship). However, BD NN cages have a much larger fraction of unoccupied space. In addition to that arising from the atomic size mismatch described above, a BD NN cage is also missing one entire atom. To account for the additional relaxation caused by the missing atom, an additional $\varepsilon_j^i / (3Z_j^i)$ is added to the energy calculated using the above approximation. Fig. 2b shows the calculated NN cage energies for ideal and BD Cu NN cages in the Cu–Zr system. Also shown is the difference between ideal and BD cages with the same number of Zr atoms. This difference between ideal and BD cages is $\varepsilon_j^i / (3Z_j^i)$; a reasonable estimation of the formation energy of a BD, which should be on the order of $\varepsilon_j^i / (2Z_j^i)$ [12].

3. Application to Zr-based metallic glasses

3.1. BDs and atomic structure

Fig. 3 shows the distribution of ideal and BD NN cages for Cu–Zr and Ni–Zr alloys at a composition of $X_{\text{Zr}} = 0.5$, calculated at 773 K. The BD NN cage probability distributions show a similar shape to those for ideal NN cages. The total and partial equilibrium concentrations of BDs present in each system are summarized in Table 2 (Table 2 also presents the equilibrium concentration of defects in alloys of different compositions, calculated at their respective T_g , and will be discussed below). The Cu–Zr alloy has an equilibrium BD concentration of 3.6×10^{-2} , and a partial concentration around Cu that is about twice that around Zr atoms. The total concentration of BDs in the Ni–Zr alloy, 2.17×10^{-2} , is less than that of Cu–Zr, and the difference between those around Ni and Zr atoms is smaller. Differences in the calculated partial BD concentrations of each species are not surprising. The energetic cost of creating a BD should be related to the enthalpy, or energy cost, of breaking a bond between a central atom and a NN, and the BD concentration will scale this energy. For $\text{Cu}_{50}\text{Zr}_{50}$ at 773 K, the average bond energies between a central atom and NN are -0.42 and

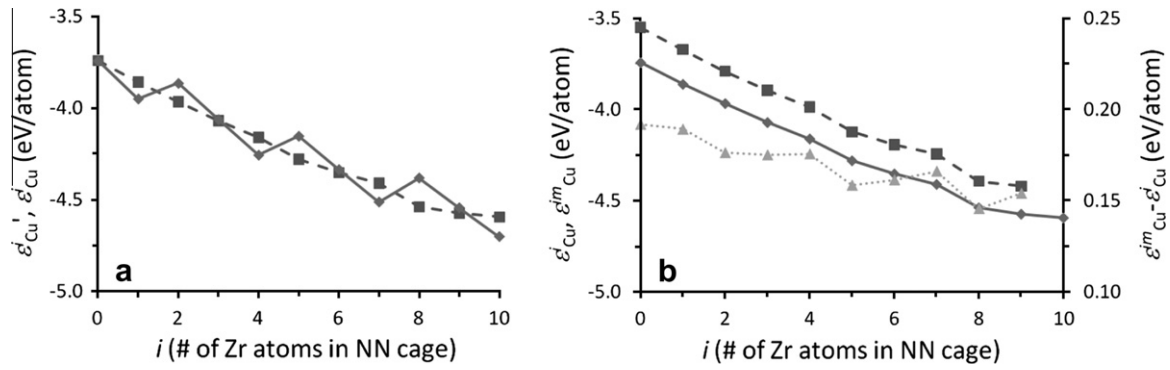


Fig. 2. (a) The enthalpy of Cu NN cages in the Cu–Zr binary system as a function of i without accounting for structural relaxation (solid); and when $-a \cdot \delta_j^i \cdot \epsilon_j^i$ is used to estimate the energy of structural relaxation (dash). (b) The calculated enthalpies of ideal, ϵ_j^i (solid), and BD, ϵ_{Cu}^{im} (dashed), Cu NN cages in the Cu–Zr system as a function of i . The enthalpy difference between ideal and BD NN cages with the same number of Zr atoms, also shown (dotted), is $\sim 0.3\epsilon_j^i$, the estimated energy of a ghost bond [17]. Calculations are performed at 773 K with $\alpha = 0.3$.

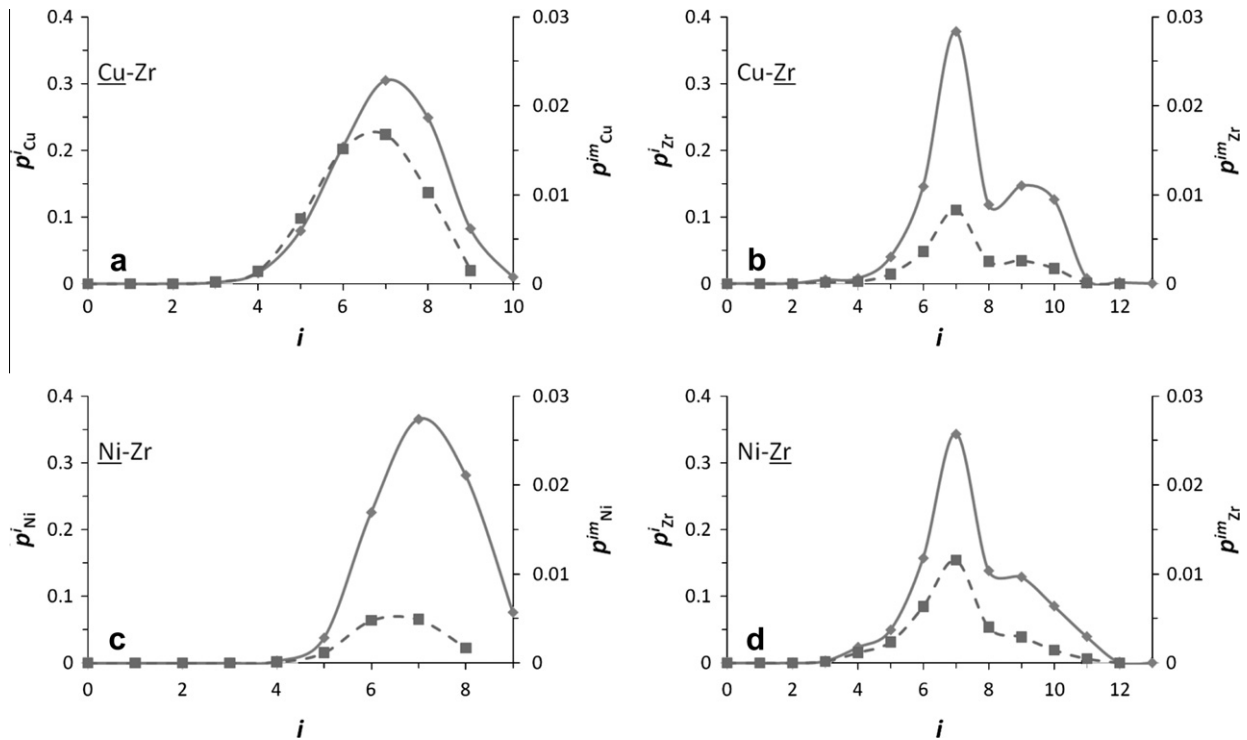


Fig. 3. Probability distributions of ideal NN cages, p_j^i (solid), and BD NN cages, p_{Cu}^{im} (dashed), for a composition of $X_{Zr} = 0.5$, for (a) Cu and (b) Zr central atoms in the Cu–Zr system, and for (c) Ni and (d) Zr central atoms in the Ni–Zr system. All calculations are performed at a temperature of 773 K.

Table 2

Equilibrium concentration, m^e , of BDs in an alloy of composition $X_{Zr} = 0.5$ at 773 K in the Cu–Zr and Ni–Zr systems, along with the partial concentrations, m_M^e ($M = \text{Cu}$ or Ni), and m_{Zr}^e , surrounding each individual species.

	$m^e (\times 10^{-2})$	$m_M^e (\times 10^{-2})$	$m_{Zr}^e (\times 10^{-2})$
Cu ₅₀ Zr ₅₀	3.64	5.25	2.03
Ni ₅₀ Zr ₅₀	2.17	1.27	3.06

−0.47 eV for Cu and Zr, respectively; and −0.51 and −0.53 eV for Ni and Zr, respectively, for Ni₅₀Zr₅₀. The higher BD concentration around Ni than Zr in Ni₅₀Zr₅₀, despite the weaker bond strength, may be because of the

large negative heat of mixing between Ni and Zr. From Fig. 3, Ni atoms are surrounded primarily by Zr atoms. Ni–Zr bonds are more stable than Zr–Zr, making it more likely a BD will form from a Zr–Zr bond than from a Ni–Zr one.

The inclusion of BDs in CAM can be used to study the extra volume associated with the amorphous structure. The original FV model of a liquid phase defines any excess volume above a certain minimum atomic volume (close to that of a crystal) as free volume, i.e., it can be moved or redistributed with no energy of migration. When applied to a glassy phase, this excess volume is defined as a deviation from ideal dense random packing (DRP); because of

the solid nature of the glass, however, its migration requires an activation energy. In both cases, there is no clearly defined atomic structure. Using CAM, an ideal amorphous phase is considered to be a set of ideal NN cages (no BDs) with densely packed configurations. Deviations from this ideal structure are the CAM equivalent of “extra” volume in the FV model. These deviations occur in the form of BD NN cages, or as ideal-type NN cages with low packing efficiencies. Additional contributions to the extra volume in the glassy phase also arise via geometrically required defects for MRO, but cannot be treated in the current model using only first NNs.

For Cu–Zr binary glasses, if a BD is assumed to have a volume of $\sim 1/5$ of an atomic volume, the 2–5% equilibrium concentration of BDs listed in Tables 2 and 3 suggest 0.5–1% in excess volume in the glassy structure, compared to a defect-free amorphous structure. The contribution to extra volume from ideal-type NN cage packing efficiency is around $\pm 0.4\%$ for the three compositions in Table 3. The extra volume is actually decreased by efficient ideal NN cage packing in the alloy $\text{Cu}_{64}\text{Zr}_{36}$, which has been shown experimentally to possess the highest glass-forming ability (GFA) in the Cu–Zr binary system. Metallic glasses typically have densities of 97% that of their crystalline counterpart, with alloys having the highest GFA approaching 99% [11]. Combining the two sources above, CAM yields an estimate of 0–2% excess volume in the amorphous structure; a good first approximation of the experimentally determined extra volume in metallic glasses.

3.2. BD concentration and glass transition

The properties of a metallic glass are governed not only by the thermodynamics of the system, but also by kinetics. The dependence of the glass transition temperature, T_g , on sample processing history and differential scanning calorimetry (DSC) heating rate in experiments is one example of this behavior. The introduction of defects into the CAM of a metallic glass allows the kinetic processes associated with the glass to be examined. If a BD is assumed to be the primary transport mechanism [14], insight can be gained into the role that kinetics plays in the glass

transition. Table 3 shows the equilibrium concentration of BDs, m^e , and the partial concentration surrounding Cu/Ni and Zr atoms, m_M^e ($M=\text{Cu}$ or Ni) and m_{Zr}^e , respectively, for various compositions in the Cu–Zr and Ni–Zr systems, each calculated at that composition’s corresponding glass transition temperature. The T_g values of 773, 693 and 653 K for Cu–Zr alloys of compositions $X_{\text{Zr}} = 0.36$, 0.5 and 0.6, respectively, are experimentally determined in the present work from an average of at least three DSC scans for each composition, following synthesis of the glasses by melt spinning at 30 m s^{-1} in a He atmosphere. The Ni–Zr alloy glass transition temperatures are taken from the work of Jiang et al. [18].

Notice in Table 3 that both m^e and m_M^e vary by a factor of 2 or more at T_g for the two systems. Looking at m_{Zr}^e , however, reveals that the concentration of BDs surrounding Zr atoms is roughly constant at T_g for a given system, regardless of composition. For Cu–Zr alloys this “critical” concentration is $1.1\text{--}1.3 \times 10^{-2}$, and for the Ni–Zr system it is found to be $2.3\text{--}2.5 \times 10^{-2}$. Although these values are for a glass in metastable equilibrium, while experimentally prepared alloys are removed from this equilibrium state, this constant value indicates a strong correlation between the calculated defect concentration and the glass transition temperature. These critical values calculated for the Cu–Zr and Ni–Zr systems are also comparable to the equilibrium vacancy concentration found in a crystalline material near the melting temperature, i.e., $\sim 10^{-3}$ [20].

It has been suggested that T_g will correspond to a temperature where some characteristic concentration of defects is reached that will allow for structural relaxation and increased atomic mobility [12]. The equilibrium BD concentrations given in Table 3 demonstrate that it is not the total concentration of BDs that reaches a critical value at T_g ; rather, it is the concentration surrounding a specific species, here Zr for both systems. The Zr atoms must reach a certain concentration of BDs for significant atomic movement, and thus the glass transition, to occur. This hypothesis is in agreement with the argument that atoms of smaller size diffuse at the same rate as larger ones in a multicomponent metallic glass, and thus the larger atoms (Zr here), dictate the diffusivity and ultimately the glass transition [21].

Assuming that the glass transition occurs when the concentration of defects surrounding Zr atoms reaches some critical value, it is possible to estimate the expected values of T_g as a function of composition. Using an average value of m_{Zr}^e in Table 3, an expected glass transition temperature is estimated by calculating the temperature at which m_{Zr}^e reaches this critical value. Fig. 4 plots this temperature as a function of composition for the Cu–Zr and Ni–Zr systems, and shows a window of $\pm 25 \text{ K}$ from this temperature. Also plotted are experimentally determined values of T_g for Cu–Zr [22–25] and Ni–Zr [18,19] alloys. There is good agreement between the predicted glass transition temperature and those determined experimentally. T_g increases with decreasing Zr

Table 3
Equilibrium concentration of BDs, m^e , and partial concentration surrounding M ($M=\text{Cu}$ or Ni) and Zr atoms, m_M^e , calculated at T_g for various compositions in the Cu–Zr and Ni–Zr systems.

Cu–Zr	T_g (K)	$m^e (\times 10^{-2})$	$m_M^e (\times 10^{-2})$	$m_{\text{Zr}}^e (\times 10^{-2})$
$X_{\text{Zr}} = 0.36$	773	4.84	6.94	1.11
$X_{\text{Zr}} = 0.5$	693	2.51	3.76	1.26
$X_{\text{Zr}} = 0.6$	653	1.66	2.30	1.23
Ni–Zr				
$X_{\text{Zr}} = 0.34$	858	2.85	3.15	2.26
$X_{\text{Zr}} = 0.36$	833	2.55	2.68	2.32
$X_{\text{Zr}} = 0.5$	733	1.74	1.00	2.48
$X_{\text{Zr}} = 0.6$	693	1.59	0.54	2.29

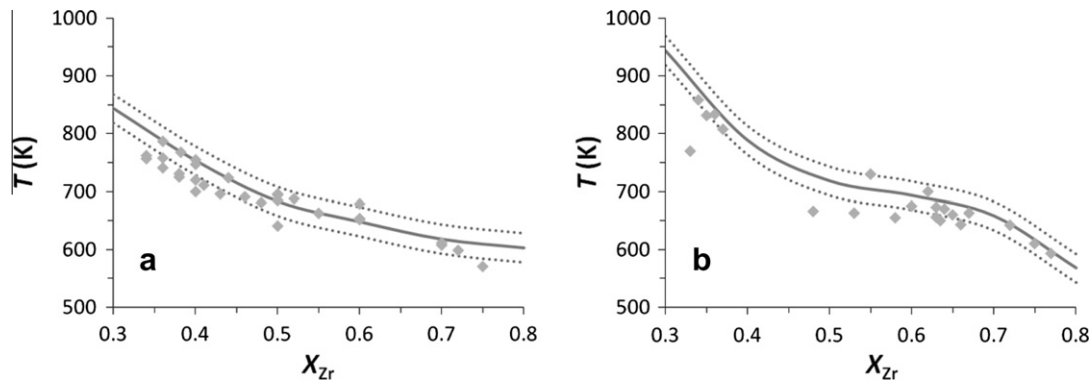


Fig. 4. Predicted glass transition temperature as a function of composition (solid), calculated using the average values of m_{Zr}^e at T_g , found in Table 3, for (a) the Cu–Zr and (b) the Ni–Zr systems. The dotted lines are ± 25 K, yielding a 50 K window for expected T_g s. Also shown are experimentally determined values of T_g for several compositions (diamonds).

content for both Cu–Zr and Ni–Zr alloys. At higher Cu and Ni concentrations, e.g., $X_{Zr} < 0.5$, the predicted glass transition begins to rise rapidly. The likely reason is that, although m_{Zr}^e remains roughly constant, m_M^e is becoming high, of the order of several per cent for Cu. There is a correlation effect between the mobility of Cu/Ni and Zr atoms. Most Zr atom NN cages will contain one or more Cu atoms with a BD, and the mobility of Zr atoms will be affected by the mobility of Cu atoms. Therefore, at composition extremes, the BD concentration surrounding both species becomes important. This reiterates the idea that T_g is a property related to both the thermodynamics and kinetics of the system. It is determined by a balance between defect concentration, primarily a thermodynamic property, and the atomic mobility of all species in the system.

3.3. Extension to higher-order systems

CAM can readily be applied to ternary and higher-order alloy systems. However, the model becomes increasingly complex when an additional component is added—primarily because of the rapidly increasing number of NN cages that must be considered. For instance, in the Cu–Zr binary alloy, there are 25 (11 Cu and 14 Zr) ideal-type NN cages and 23 BD cages (see Table 1), or 48 in total. If Al is added as a ternary element, the number of ideal NN cages alone increases to ~ 70 for Cu, ~ 100 for Zr, and ~ 80 for Al, or by a factor of 10 compared to binary Cu–Zr. Adding components to CAM also increases the number of constraints, Eq. (16). A second mass balance constraint, Ψ_3 , for C atoms is needed; and a second Lagrange multiplier similar to λ in the above equations will be needed to determine the NN cage probabilities. Finally, if BDs are included in the model, Ψ_4 and Ψ_5 become more complex; and solving for λ_4 and λ_5 (or λ_6 and λ_7) becomes more difficult. These issues can be overcome by utilizing increased computer power and/or minor simplifications. Extension of CAM to ternary and quaternary alloys is demonstrated in Ref. [6]; it will also be the subject of a future report.

4. Conclusions

The presence of defects, termed bond deficiencies (BDs), was introduced into the CAM model of a metallic glass. A single BD is defined as the absence of one atom from the ideal NN cage surrounding a central atom. The defect is similar to a vacancy in a crystalline material, though the energy and volume cost of formation is much smaller. Like vacancies, BDs are thermodynamically stable entities, and an equilibrium concentration of BDs can be calculated at a given temperature. The calculated equilibrium BD concentration was found to be $\sim 10^{-2}$ at the glass transition temperature for Cu–Zr and Ni–Zr binary metallic glasses. This concentration is similar to the vacancy concentration in a crystalline material at its melting temperature. The partial concentration of BDs surrounding each species was found to be dependent upon the average bond energy between a central atom and its NNs. The larger this energy, the larger the energetic cost of creating a BD.

In studying equilibrium BD concentration as a function of composition for the two Zr systems, the concentration of BDs surrounding Zr atoms was found to be relatively constant at the glass transition temperature. This critical concentration is found to be $1.1\text{--}1.3 \times 10^{-2}$ and $2.3\text{--}2.5 \times 10^{-2}$ for Cu–Zr and Ni–Zr glasses, respectively. From this critical defect concentration, expected glass transition temperatures were calculated as a function of composition. The calculations correlated well with experimentally determined glass transition temperatures for both the Cu–Zr and Ni–Zr systems.

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