DETERMINATION OF GLASS-FORMING ABILITY OF

METALLIC GLASSES USING ATOMISTIC MODELING

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ABSTRACT

Metallic glasses are a relatively new class of engineered material with many unique properties including high yield strength and easy formability. However, they are currently limited by the fact that only limited compositions are known to form metallic glasses, which often contain expensive components. In this work, a computational tool to assess the glass-forming ability of an alloy was developed to help overcome that issue. Through calculating the viscosity of the liquid state and the fraction of icosahedra, we are able to classify alloys by the relative amount of diffusion and driving force for crystallization in the liquid state. The first test of this system on the copper-zirconium binary system identified Cu-35.7at%Zr and Cu-54at%Zr as the best glass-forming alloys, which is consistent with experimental findings. This tool was designed in such a way to be applicable to many different alloy systems and to be simple enough to enable automated testing of many possible compositions.

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1   INTRODUCTION AND OBJECTIVES

1.1   *Motivation*

Metallic glasses are a unique class of materials for the fact that they are metallic, but lack the crystalline order of conventional metals. Under typical circumstances, metals form crystals when cooled from the liquid state that rapidly grow to create a fully-ordered structure. It was only found relatively recently (1960) that it was possible to cool a metallic liquid fast enough that it forms a solid and keeps its amorphous structure [1]. The first glasses needed to be cooled at exceptionally high rates in order to form in the amorphous state, which limited the casting thicknesses to less than 1 mm. In the mid-1970s, compositions were discovered that could be formed into larger, more commercially-useful thicknesses [2]. Since then, there has been much research into how to develop these "bulk metallic glasses" for use commercially.

The unique structure of metallic glasses leads to many properties that are superior to conventional metal alloys and ceramics. In particular, the absence of long-range order results in metallic glasses being much stronger than standard alloys because deformation by crystal plane slip is not available. In addition to strength close to that of ceramics, these materials have inherently high fracture resistances, which make them interesting as structural materials [3]. One of the other exciting features of an amorphous structure is that no volume change occurs during the transformation from liquid to solid states. For that reason, one can process metallic glasses with techniques usually only reserved for plastics [4], such as blow-molding as shown in figure 1.1.

Figure 1.1:   Bulk metallic glass formed by blow molding [4].

The exceptional mechanical properties of metallic glasses along with easy formability make these materials promising choices for many applications. For instance, the high yield strength of the alloy gives it very good wear resistance, which makes them an excellent choice for industrial wear coatings [3]. This exceptional wear-resistance and low elastic modulus also yields improved bio-compatibility for hard-tissue prosthesis applications [5]. In addition, metallic glasses have also been used for high-performance sporting equipment, fine jewelry, and defense applications [6].

While the amorphous structure of these materials gives them superb properties, it is also their key detriment. Because metals are most stable in a crystalline arrangement, bulk metallic glasses are far from equilibrium. Consequently, the fast cooling rates required to bypass crystallization limit metallic glasses to casting thickness of under 8 cm even for the best alloy compositions [7]. Furthermore, there are not many known metallic glass alloys and many contain expensive components [1]. For both of those reasons, there has been great interest in finding new alloys and developing rules to select the best alloy compositions.

Over the past several decades, a series of empirical rules have been developed to aid in the selection of alloys. For example, it is desirable to find a stable liquid composition through locating low-melting eutectics [9,10]. Liquids that stay stable to such a low temperature would therefore have slower diffusion in the supercooled liquid, thereby stunting crystal growth. Also, it has been found that bulk metallic glasses have densities close to their crystalline counterparts, which indicates that the packing of atoms in this amorphous structure is very efficient and energetically stable [11]. The other main empirical rule is therefore to find a combination of atomic components that can be packed into an efficient, non-crystalline structure [9,11].

While these empirical rules are effective in locating the general region were metallic glasses are formed, it is still difficult to locate the optimal composition experimentally. In several recent papers, finding the best alloy required an incremental search of many different compositions [12,13]. This method is successful, but can prove expensive and time-consuming. Each test of a metallic glass requires high-purity materials and proper calibration of the casting equipment to be successful. Developing a computational approach to find a best-guess of an optimized composition could drastically reduce the number of experimental compositions needed to be fabricated and tested. With a sufficiently simple, widely-applicable computational method, it would be possible to effortlessly and cheaply scan compositions to give experimentation a better starting point.

1.2   Other Empirical Rules

Outside of the two main rules of alloy selection (deep eutectics, efficient packing) there are other experimental factors that are known to correlate with glass-forming ability. Three of the most important factors are: reduced glass transition temperature (T_{rg}), fragility, and stability in the supercooled liquid.

Reduced glass-transition temperature (T_{rg}), also called the Turnbull criterion, is based on a nucleation-growth argument and is defined as the ratio between the glass transition temperature (T_g) and the liquidus temperature (T_l) [10]. The basis of this idea is that the nucleation rate in a glass is not just dependent on the degree of undercooling (cooling below the melting temperature), but also the amount of diffusion in the liquid. By making the assumption that there is a temperature where the diffusion in a liquid stops completely, it was possible to express the nucleation rate as a function of that temperature (assumed to be the glass-transition temperature), the melting temperature, and the current temperature of the

liquid [8]. With that relationship, it was possible to show that homogeneous nucleation is suppressed for $T_g/T_l \geq 0.66$ [8]. This analysis is also the rationale for finding glasses with low melting temperatures.

The fragility of a liquid is a measure of how its viscosity changes as a function of temperature. The main concept behind tying this parameter to glass-forming ability is that liquids with a high viscosity have slow kinetics, which inhibits the growth of crystals [1]. A glass with a low fragility parameter slowly changes viscosity as temperature is increased past the glass-transition temperature [14]. Consequently, liquids with a lower fragility reach a higher viscosity (with slower kinetics) at a higher temperature upon cooling and should therefore form crystals less easily. This factor has been extensively studied in metallic glasses, and is experimentally known to correlate with glass-forming ability [15].

The study of stability in undercooled liquids started before 1952 [16] but has only been discussed in terms of metallic glass forming recently [17,18,19]. It was originally proposed that icosahedral ordering in the liquid are efficiently-packed and therefore energetically stable clusters that serve to stabilize the liquid by serving as an energetic barrier against nucleation [16]. These types of clusters are also known to lead to slow dynamics in the liquid [18]. Based on these ideas, it can be assumed that a large fraction of icosahedra in the liquid state can allow for a metal to more easily bypass crystallization.

1.3   Currently Available Computational Methods

There have already been several different studies that attempted to characterize glass-forming ability using computational tools [20-29]. Most commonly, metallic glasses are studied using various atomistic modeling strategies. This type of simulation is well-suited for this problem because the amorphous structure of metallic glasses implies that they have no order

that persists beyond a few atoms. So, a simulation on the size scale of less than several nanometers should be able to capture most key behaviors. With molecular dynamics, in particular, it is possible to model the time-evolution of a collection of atoms at a specified temperature or for a specific temperature profile. In this way, one can create a model of a metallic glass by simulating the melting and quench process from experiment.

The key issue with atomistic modeling is that it is only computationally feasible to simulate timescales of less than one microsecond or so because the time increments have to be small enough to follow the thermal oscillations of the atoms (less than 10 fs). Calculating critical cooling rate, which describes the slowest cooling rate that bypasses crystallization, would require times scales on the order of one millisecond, which is currently impossible (or at least highly unpractical). For that reason, researchers have decided to adopt simplified hard-sphere systems [20,21] or to use a structural analysis to find efficient, non-crystalline structures [22,23,24] in order to characterize glass-forming ability. Of these, only one attempted to determine the optimal alloy in a real system [24], but only searched regions within 1-2 at% of known glass-forming compositions. In all cases, only the structure was studied and no consideration was made for the dynamics of the system.

Several other computational studies used computational thermodynamics to find an optimal glass-forming composition [25,26,29]. With this technique, it is possible to quantitatively predict the energetic driving force for nucleation of a crystal in the liquid. In one study, it was found that this driving force alone is not an accurate prediction of glass-forming ability because the most stable glasses did not necessarily have the best driving force [25]. For that reason, liquid fragility was used to introduce kinetics into a combined expression for glass-forming ability. This study did succeed in being able to locate the

optimal glass-forming alloys in a system, but required fragility to be measured experimentally.

A third computational method used to locate glass forming compositions is based on finding alloy compositions that can pack efficiently into non-crystalline arrangements [11]. Existing metallic glass compositions are known to have compositions that are close to what can be predicted using this "cluster-packing" scheme [11]. This strategy can then be applied to assist in identifying new compositions [25,27]. One of the key issues with this strategy is that it only considers the simple packing of hard spheres and does not take bonding between the atoms into account, which is known to be a key factor in glass-forming [28].

1.4　Objective

The objective of this work is to develop a method of predicting glass-forming ability in metallic glasses using only computational techniques. This system must be flexible enough to apply to new systems. The main impact of this work will be the creation of a tool to accelerate the experimental discovery of metallic glass compositions and to enable the study of the mechanisms behind glass-forming in metals.

2   COMPUTATIONAL APPROACH

2.1   Modeling Technique

Molecular dynamics (MD) was selected because it can be used to study compositions across many different alloy systems. This simulation technique (outlined by figure 2.1) is based on simulating the motion of individual
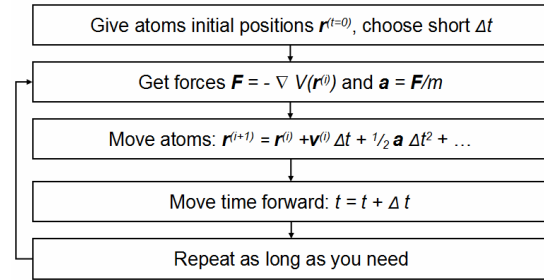
Give atoms initial positions $r^{(t=0)}$, choose short Δt
Get forces $\boldsymbol{F} = -\nabla\, V(r^{(i)})$ and $\boldsymbol{a} = \boldsymbol{F}/m$
Move atoms: $r^{(i+1)} = r^{(i)} + \boldsymbol{v}^{(i)}\,\Delta t + \frac{1}{2}\,\boldsymbol{a}\,\Delta t^2 + \dots$
Move time forward: $t = t + \Delta t$
Repeat as long as you need

Figure 2.1:   Flow diagram that outlines molecular dynamics [30].

atoms over the course of time. The energy and forces acting on each atom are determined by empirical functions, known as interatomic potentials, which are developed the model the physical properties of a particular species. In particular, we chose to use Embedded Atom Method (EAM) interatomic potentials because they are known to well-describe metals [32]. Another important advantage of molecular dynamics is that these potentials can be directly used for our simulations without the need for any additional, application-specific experimental measurements.

2.2   Key Parameters

With a molecular dynamics simulation, it is currently impossible to directly measure the critical cooling rate of a metallic glass. For that reason, it will be necessary to instead determine factors that are known to lead to favorable glass-forming ability. As discussed in Sec. 1.2, to prevent crystals from forming in a liquid, there needs to be a small driving force for their creation and limited atomic mobility to slow their growth. The reduced glass-transition temperature takes both of these factors into account to a limited degree, but is difficult to accurately calculate using molecular dynamics [31]. Fragility, however, can be

calculated effectively using molecular dynamics [34,38] and is known to describe the kinetics in the liquid state [1,15]. The relative magnitude of the driving force can be determined by finding the fraction of icosahedra in the liquid [16], which can be calculated easily.

2.3 Test System

For the initial test of this methodology, we chose to predict the best glass-forming composition in a copper-zirconium metallic glass system. This system was chosen for the presence of sufficient experimental data to validate against [36,37] and the availability of Embedded-Atom Method (EAM) potentials [32].

2.4 Calculation Strategy

2.4.1 Simulation Parameters

The Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was used to run the molecular dynamics simulations. Embedded-atom method potentials developed by Mendelev were used for interatomic potentials [32]. The simulation used periodic boundary conditions in all three directions and a timestep size of 2 fs.

2.4.2 Model Generation

Models of the metallic glasses were created using a technique similar to what is already common practice in the literature [23,24]. To create a model of a metallic glass, we started with a body-centered cubic copper lattice of 11,664 atoms and replaced enough copper atoms with zirconium to give the system the desired composition. The system was then thermalized at a temperature of $300\,\mathrm{K}$ and heated to $3000\,\mathrm{K}$ at $6.75 \times 10^{13}\,\mathrm{K/s}$. After $40\,\mathrm{ps}$ of

equilibration at 3000 K, the system was cooled to 1500 K at 7.5×10^{11} K/s. The model was then quenched to 200 K at a nominal rate of 1.0×10^{11} K/s in temperature steps of 32.5 K, according to the quench schedule shown in figure 2.2. The quench rate was slowed near the glass transition (approximately 625 K) to allocate simulation time where the dynamics were slowest and then sped up once the atomic mobility abruptly slows after the transition.
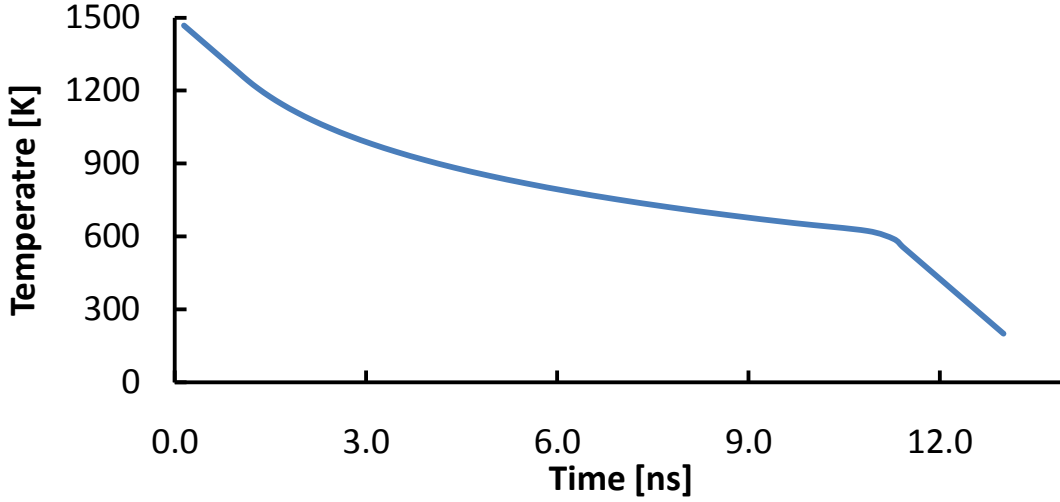
Figure 2.2:   Simulation quench schedule

2.4.3   Fragility

Fragility has been calculated on several occasions using molecular dynamics on model systems [34,38]. The method used in those papers was to calculate viscosity at several points and then to use an analytic relationship to model the temperature dependence of viscosity, which is the general principle we followed in our simulations.

Viscosity was calculated using the Green-Kubo formula,[39]

$$\eta = \frac{V}{k_B T} \lim_{s \to \infty} \int_0^s \langle \sigma_{\alpha\beta}(t)\sigma_{\alpha\beta}(0)\rangle dt \qquad (2.1)$$

for at least seven different temperatures above the glass transition. The shear stress, $\sigma_{\alpha\beta}$, as a function of time required for the Green-Kubo relation was determined in the standard way from atomic forces, positions, and simulation cell volume [34] for the different frames of an MD simulation under adiabatic conditions over 2 ns.

The Vogel-Fulcher-Tammann (VFT) relationship,

$$\eta = \eta_0 \exp\left(\frac{T_1}{T - T_0}\right) \tag{2.2}$$

was then fit to the viscosity vs. temperature data. This model was chosen because it is known to describe the experimentally-determined viscosity of metallic glasses well [41].

It was then possible to determine the fragility parameter from the fitted function using

$$m = \frac{d\log\eta}{d(T_g/T)} \tag{2.3}$$

The glass transition temperature was determined to be the point at which the viscosity is 10^{12} Pa-s, which is a convention borrowed from experiment [41].

2.4.4   Icosahedral Fraction

Studying the structure of a supercooled liquid is complicated by the fact that the liquid structure changes as a function of temperature [18]. However, since the atomic structure freezes below the glass-transition temperature and the structure right above that transition is what is of interest, the glass structure at low temperature can be studied to reveal the liquid structure near the glass transition. Therefore, the structure at 300 K, generated from quenching, was first relaxed to remove all thermal vibrations and then analyzed for each model.

The first step of the local order analysis was identifying the nearest-neighbors, which was based on a Voronoi tessellation analysis found in the literature [42]. In short, Voronoi

tessellations partition the space around a set of nodes such that each node is surrounded by a polyhedral cell containing the space that is closest to that point. Neighbors of a node can be identified by finding nodes in an adjacent cell that shares a common face [43].

One issue with this method is that it will identify false neighbors, which is often addressed by removing neighbors that have the smallest shared faces [19,42]. In this work, we propose selecting neighbors by using the assumption that nearest neighbors are atoms that would contact if all atoms were hard spheres. If we assume the atoms are spherical (which is assumed in our EAM potentials), the point at which they would contact lies on a line between the centers. A Voronoi face intersecting that line then indicates that the point of contact actually exists in the space closest to each atom.

Once a neighbor connectivity map was produced, the local order around each atom was classified by the number of bonds each neighbor forms with other neighbors of that atom. In this scheme, an icosahedron has twelve neighbors each connected to five others. The degree of icosahedral order was presented as a fraction of number of atoms with icosahedral neighbor coordination.

2.5   *Energy-Weighted Averaging*

For each tested composition, the fragility parameter and icosahedral ordering were determined for 15 independent simulations. For each simulation, a different random distribution of zirconium atoms in the initial copper lattice was used. The results were averaged with weighting with respect to their total energy (potential and kinetic) at 800 K using a Boltzmann average:

$$\langle P \rangle = \sum_i e^{\frac{E_i}{kT}} P_i \Big/ \sum_i e^{\frac{E_i}{kT}} \tag{2.4}$$

It is known through statistical mechanics that the probability of a system being a certain state is dependent on the Gibb's factor [44]. And so, the property calculated from each system should be weighted by the probability of finding a system of that specific composition in that configuration.

2.6 Combination of Factors

We also propose a method for combining the kinetics and driving force information to create a single figure of merit. To do so, the average value for each parameter across all compositions tested was calculated. With this, it was possible to calculate the "average improvement" of an individual composition with respect to the system average. To do so, a figure of merit (V) that describes the improvement in glass-forming ability over the average was calculated using:

$$V = \alpha \frac{\overline{m}}{m} + \frac{Icos}{\overline{Icos}} \qquad (2.5)$$

With this relation, the weight factor (α) can be used to tune the relative contribution of each effect on the figure of merit.

3   CALCULATION RESULTS

The fragility and icosahedral fraction were calculated for ten copper-zirconium systems ranging from 35.7 at% to 60 at% zirconium. This particular range was selected due to the presence of experimental data for fragility [36]. Table 3.1 lists systems that were chosen for this computational study.

Table 3.1:   Copper-Zirconium systems used and number of iterations for each simulation. An underline indicates the systems for which experimental data is available.

Number	Zr [at%]	Iterations	Number	Zr [at%]	Iterations
1	35.7	15	6	50	15
2	38.2	15	7	52	15
3	40	15	8	54	15
4	44	15	9	57	15
5	47	15	10	60	15

3.1   Fragility Calculations

Viscosity was calculated for at least seven temperatures for all 150 MD runs, shown in table 3.1, and the VFT model was least-squares fitted to each. An example of this is shown in figure 3.1. A key limitation of the viscosity calculation is that it is computationally unfeasible for viscosities over 10 Pa-s due to the simulation time limitations. For that reason, it was necessary to extrapolate to 10^{12} Pa-s in order to calculate fragility.
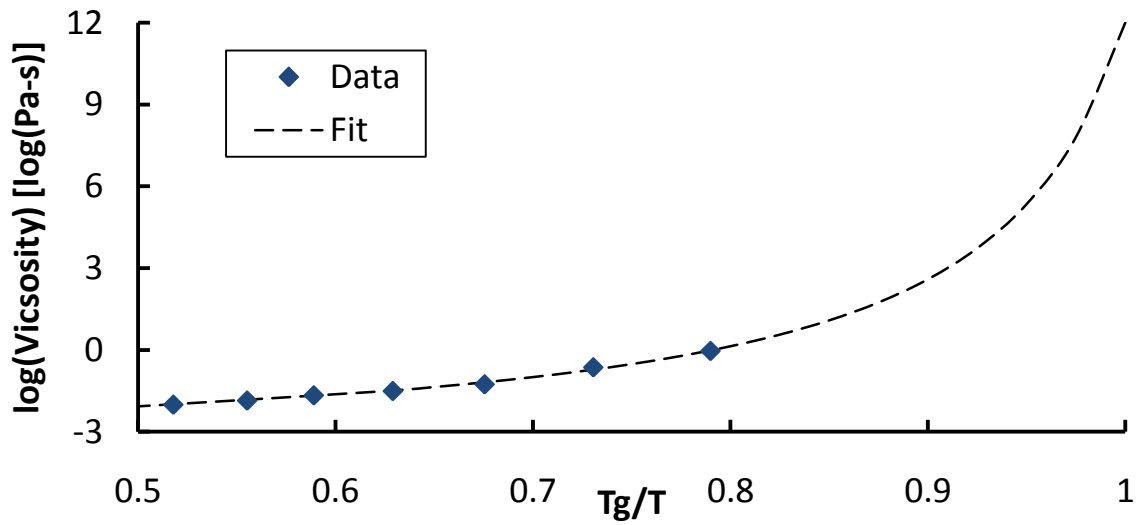
Figure 3.1: Example of the viscosity calculation results and a fit using the VFT equation.

Figure 3.2 shows the calculated fragility in comparison to experimental values [36]. Fragility is known to vary with quench rate [45], which could cause the magnitude of the experimental and computational values to be different. In the case of glass-forming ability, only the relative magnitude between the different systems is important. For that reason, both results were normalized so that the fragility at Cu-44at%Zr was equal to 1.0. The error bars on figure 3.2 are the standard error of the mean for the calculated fragility.
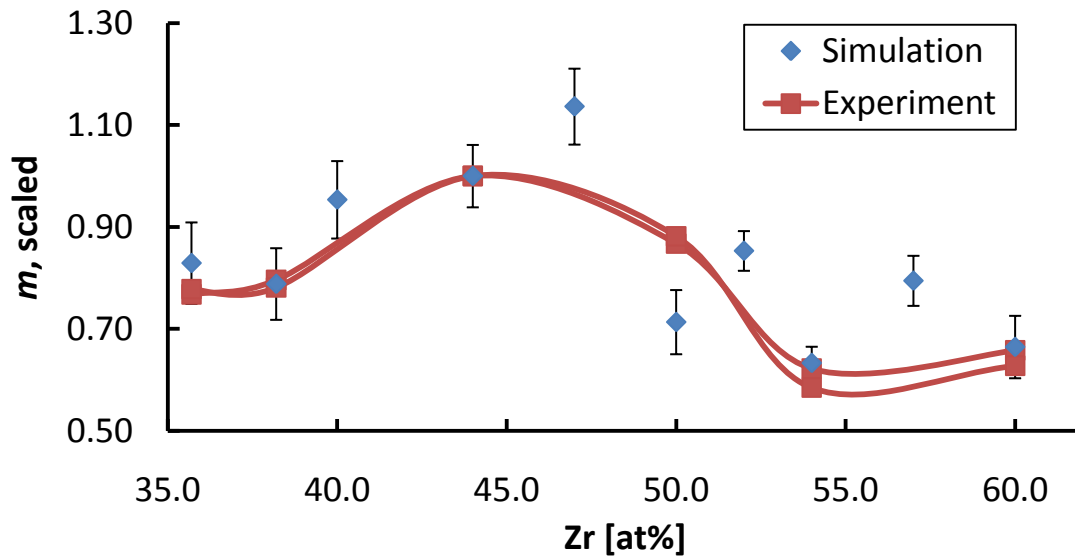
Figure 3.2: Calculated and experimental [36] fragility (*m*) for copper-zirconium metallic glasses with varying composition. The fragilities are scaled.

3.2   Structural Analysis

For each model, the polyhedra formed by the neighbors around each atom were assigned an index of the form $\langle v_3, v_4, \ldots, v_n \rangle$,, where v_n is the number of neighbors with *n* bonds. The total fraction of the atoms with each index was calculated, as shown in figure 3.3. The fraction of icosahedra was determined by the fraction of atoms that have a nearest-neighbor coordination with a $\langle 0,0,12,0 \rangle$ index.
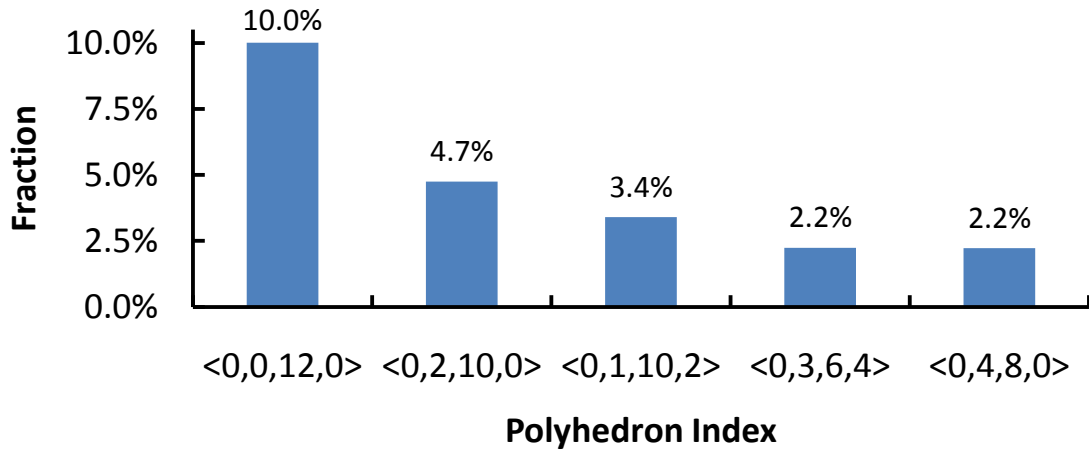
Figure 3.3: Example results from local order analysis: fraction of most common nearest-neighbor polyhedra by shape.

Figure 3.4 shows the icosahedron fraction for each composition tested. The difference between the iterations of each composition is rather small, so the standard error of the mean is particularly low in this measurement.
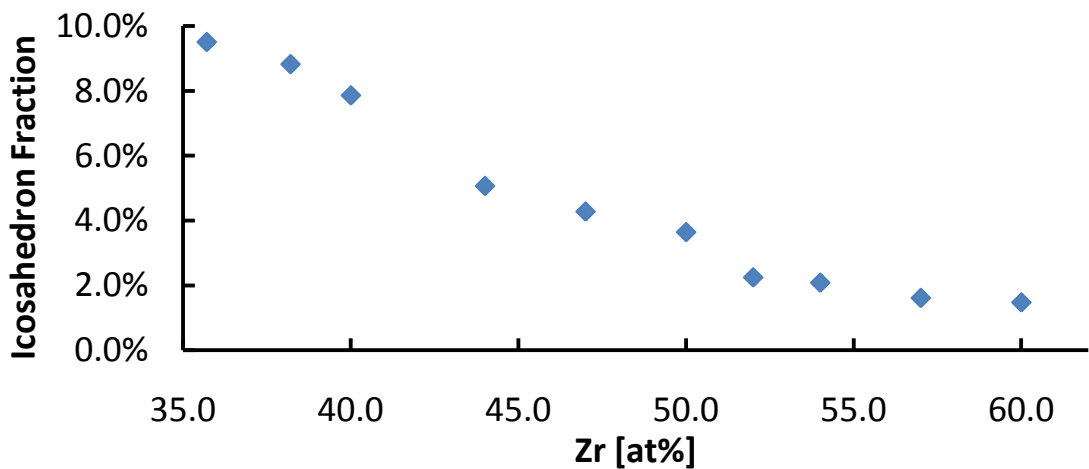
Figure 3.4: Calculated icosahedron fraction as a function of composition in copper-zirconium system.

3.3   Combination of Results

Figure 3.5 shows the results of the figure of merit defined in equation 2.5. The value of the weight constant (α) was varied from 0.1 to 10 to change the relative contribution of the fragility in glass-forming ability.

Figure 3.5:   Figure of merit for glass-forming ability from Eq. (2.5) with varied weight for fragility.

4   DISCUSSION

4.1   Fragility Calculation

As shown in figure 3.1, the VFT relationship (equation 2.2) seems to describe the calculated viscosity data well. In this particular fit, the correlation coefficient between the function and calculated data was 0.996. At least from a qualitative standpoint, the other fits were equally well-described by the VFT model. This indicates that the liquid in simulation was behaving in a manner close to what is seen experimentally in metallic glasses [41].

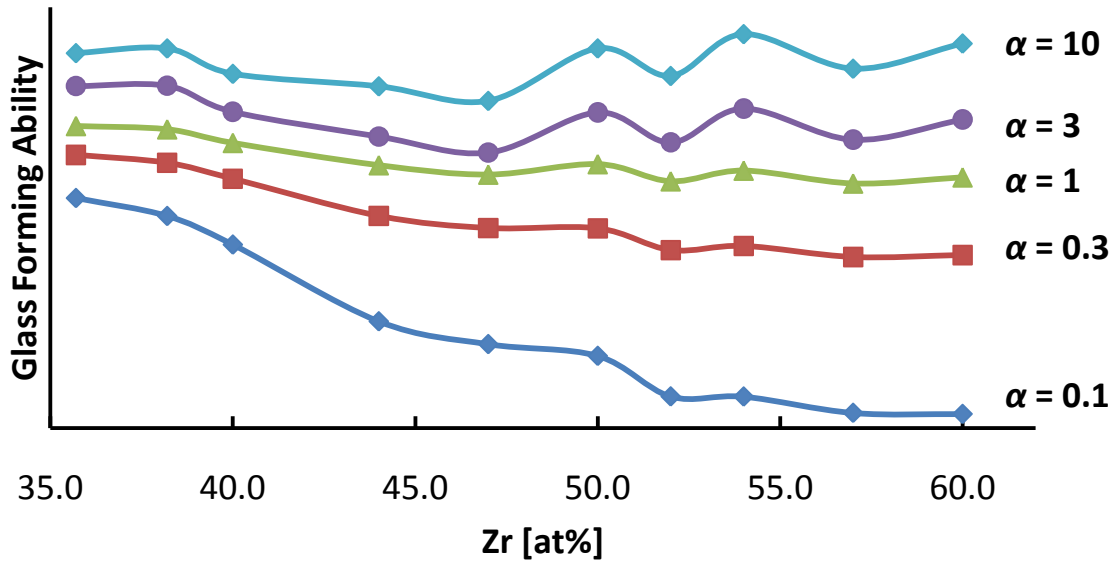The relative magnitudes between compositions for the experimental and calculated results are similar (correlation coefficient of 0.858), as shown in figure 3.2. The relative magnitudes of fragility between compositions are desired for comparing the possible glass-forming ability, which makes the actual values not particularly important. With that notion in mind, the fragility calculation was able to identify the local extrema well by correctly locating a maximum near 45 at% Zr zirconium and two minima near 36 at% and 55 at% Zr. So, it is reasonable to assume that we can rely on this technique to identify the best candidate glasses based on fragility.

In terms of the actual values, the calculated fragilities are roughly 2.5-3.5 times higher than experimental values. This difference can be easily explained by the extreme quench rates used in the simulations. Because the fragility is known experimentally to increase with quench rate [45], it is not surprising that the calculated fragilities are much higher since the quench rates are more a factor 10^5 faster. One of the assumptions in this work must be that the quench rate dependence of fragility is similar for all samples. It would be particularly difficult to test this assumption because of the computation time required to simulate any quench rates slower than what is currently used. A simulation of a quench rate

of 10^{11} K/s, which was used in this study, requires approximately 35 hours to complete on 20 processors. While it would not be impossible to extrapolate to quench rates used experimentally (less than 10^7 K/s [1]), it may not be meaningful if the slowest computational rate is several orders of magnitude higher.

4.2   Structural Analysis

The structural analysis shows that in the range tested, the fraction of icosahedra monotonically increases with increasing copper fraction, as shown in figure 3.4. To date, there have not been experimental studies that have attempted to quantify the icosahedron fraction as a function of composition in the copper-zirconium system. The closest to this so far is a study that constructed atomistic models to fit structural information of copper-zirconium liquids derived from x-ray analysis [18]. In this study, they were able to confirm the presence of ordering characteristic of icosahedra, but did not attempt to locate entire icosahedra or to characterize the change in behavior as a function of composition. While there is no experimental data present to confirm this trend, an increase in icosahedral ordering with increasing copper-fraction has been found in another computational study [24]. With those two facts in consideration, it is reasonable to believe that the results from the structural analysis are acceptable.

4.3   Computational Requirements

Running the simulations to generate the required data for a fragility calculation and structural analysis for a single iteration requires approximately 96 hours of computation time on 20 processors on the Glenn Cluster at the Ohio Supercomputer Center [46]. From that point,

calculating the fragility and icosahedron fraction requires only one additional hour of processing time. Even though the scale of the computational time is large, it is easily manageable with the use of a supercomputer. And, since only slight modifications are required for changing composition and repeatedly randomizing the input structures, it was possible to be automated. Automation is a very useful tool for this class of computational problem because it ensures that all analyses are identical and limits the required amount of input from a user to manageable levels.

4.4   Alloy Selection

When taking fragility or icosahedral fraction into consideration alone, the results point to two different alloys. For instance, there are two regions of low fragility, which should have favorable glass-forming ability: <44at% Zr and ≥50at% Zr (see figure 3.2). If one were to base the selection solely on

Table 4.1:   Casting thicknesses of Cu-Zr alloys [47].

Composition	Critical Thickness [mm]
Cu35.5at%Zr	2
Cu36at%Zr	1.6
Cu40at%Zr	1
Cu44at%Zr	1
Cu55at%Zr	1.5
Cu54at%Zr	2
Cu50at%Zr	1.2

fragility, the best alloys would be those in the ≥50at% Zr range and the optimal composition is Cu-54at%Zr. This optimal alloy agrees with experimental findings, as indicated by Cu-54at%Zr being one of the alloys with highest critical casting thicknesses, shown in table 4.1. However, this method alone does not identify Cu-35.5at%Zr as the other top alloy even though it has a lower-than-average fragility.

Conversely, if one takes only take icosahedron fraction into account, Cu-35.7at%Zr would be selected as the top alloy (see figure 3.4). This also is consistent with experimental

findings, since Cu-35.5at%Zr is the other alloy with the best critical casting thickness. In this scheme, however, Cu-54at%Zr is not even in consideration for a top alloy.

It is therefore possible to conclude that neither explanation is suitable for identifying the best alloy in a particular system, as accepting solely one explanation would exclude one of the two best candidate alloys in a system. For that reason, we propose using a model that combines the two effects to create a single figure of merit to describe glass-forming ability. Using an assumption that there is a combined effect and that high performance in either factor would imply favorable glass-forming, the method we propose is to calculate how much better an alloy is on average than others in its system using equation 2.5 (repeated below for convenience):

$$V = \alpha \frac{\overline{m}}{m} + \frac{Icos}{\overline{Icos}} \tag{2.5}$$

Since the relative importance of each factor is not yet known, we have included a weight factor (α) to tune the combination. Depending on the choice of this factor, different alloys would be selected, as shown in figure 3.5 and table 4.2. When the weight factor is increased, the chosen alloy changes

Table 4.2: Optimal alloys from computational selected by combination method. Weight factor indicates varying importance of fragility.

Weigh Factor (α)	Best Alloy
0.1	Cu-35.7at%Zr
0.3	Cu-35.7at%Zr
1	Cu-35.7at%Zr
3	Cu-38.2at%Zr
10	Cu-54at%Zr

from Cu-35.7at%Zr to Cu-54at%Zr as the importance is shifted from icosahedron fraction to fragility. The predicted best alloy composition is consistent with experimental values except for weight values near three. Even so, the incorrect alloy that is predicted (Cu-38.2at%Zr) is within 3 at% of an optimal alloy. A good point of future research would be to find a relationship that would indicate both alloys as having close to identical glass-forming ability.

At least by being able to identify both separately, the combined fragility/icosahedron fraction method is effective in at least the copper-zirconium binary system.

4.5   Advantages of Method

Our new method is an improvement of existing molecular dynamics methods because it includes consideration for kinetics and is proven to work on a real system. In general, the use of molecular dynamics is advantageous because it allows this method to be quickly adapted to other systems. The only requirement is that interatomic potentials are available, for which there are several databases [33,48].

5   SUMMARY

Metallic glasses are interesting engineered materials because of their atomic structure that is far from equilibrium. Their amorphous structure gives them higher tensile strength and opens up new processing routes that are not possible with conventional metals. However, one of the key issues of metallic glasses is that they only form in small, difficult to find composition ranges. In order to address this issue, we have developed a technique that uses molecular dynamics to determine glass-forming ability purely from computational methods. This tool will allow for the reduction in the amount of time and effort that is needed to discover new metallic glass compositions.

Our strategy for studying glass-forming ability through calculating fragility and icosahedron fraction of the liquid is based on techniques borrowed from experimental methods. Fragility, a parameter which describes the temperature dependence of viscosity, describes the speed of the kinetics in the liquid state and is known to be low in glass-forming metal alloys. It is also known that icosahedra in the liquid lead to slow dynamics and are hypothesized to serve as an energy barrier for crystallization. Through combining the results of calculating these two factors, it was possible to locate two best glass-forming compositions in a copper-zirconium binary system: Cu-35.7at%Zr and Cu-54at%Zr. Both of which are known experimentally to be the optimal glasses in the copper-zirconium system.

6   FUTURE WORK

The future goal of this project is to integrate this tool into the design of new metallic glass systems. To do so, we must first ensure that this system is effective for more complex systems. To date, this tool has also been used to identify the best glass-forming compositions in a ternary, Cu-Zr-Ti, system.

One of the other techniques being developed in this research group is a toolkit for designing metallic glasses with optimized physical properties using atomistic modeling. Currently, alloy compositions are selected without taking the ability to form a metallic glass into consideration. Eventually, we want integrate to integrate the capability of predicting glass-forming ability with the existing property optimization techniques. To do so, we need to first develop the means to compare glass-forming ability between two different alloy systems.

REFERENCES

1. Wang, W.H., C. Dong, C.H. Shek. "Bulk metallic glasses." <u>Materials Science and Engineering R.</u>44 (2004), 45-89.
2. Chen, H.S. "Thermodynamics considerations on the formation and stability of metallic glasses." <u>Acta Metallurgica.</u> 22 (1974), 1505-1511.
3. Ashby, M.F, A.L. Greer. "Metallic glasses as structural materials." <u>Scripta Materialia.</u> 54 (2006) 321-326.
4. Schroers, J. "Processing of Bulk Metallic Glasses." Advanced Materials. 22 (2010), 1566-1597.
5. Demetriou, M., A. Wiest, *et al*. "Amorphous Metals for Hard-tissue Prosthesis." <u>JOM.</u> 62 (2010), 83-91.
6. "Liquidmetal Technologies." <www.liquidmetal.com>. Accessed 15 May 2011
7. Li, Y., S.J. Poon, *et al*. "Formation of bulk metallic glasses and their composites." <u>MRS Bulletin</u>. 32 (2007), 624-628.
8. Löffler, J. "Bulk metallic glasses." <u>Intermetallics.</u> 11 (2003), 529-540.
9. Inoue, A. "Stabilization of metallic supercooled liquid and bulk amorphous alloys." <u>Acta Materialia.</u> 48 (2000), 279-306.
10. Turnbull, D. "Metastable Structures in Metallurgy." <u>Metallurgical Transactions B.</u> 12B (1981), 217-230.
11. Miracle, D.B. "A structural model for metallic glasses." <u>Nature Materials.</u> 3 (2004), 697-702.
12. Fu, Y, B Shen, H Kimura, *et al*. "Enhanced glass-forming ability of FeCoBSiNb bulk glassy alloys prepared using commercial raw materials through the optimization of Nb content." <u>Journal of Applied Physics.</u> 107 (2010), 09A315.
13. He, Q, Y-Q Cheng, E Ma, J Xu. "Locating bulk metallic glasses with high fracture toughness: Chemical effects and composition optimization." <u>Acta Materialia.</u> 59 (2011), 202-215.
14. Angell, C.A. "Formation of Glasses from Liquids and Biopolymers." <u>Science.</u> 267 (1995), 1924-1935.
15. Park, E.S., J.H. Na, D.H. Kim. "Correlation between fragility and glass-forming ability/plasticity in metallic glass-forming alloys." <u>Applied Physics Letters</u>. 91 (2007), 031907.
16. Frank, F.C. "Supercooling of liquids." <u>Proceedings of the Royal Society of London. Series A, Mathematical and Physical.</u> 215 (1952), 43-46.
17. Peng, H.L., M.Z. Li, W.H. Wang, K.M. Ho. "Effect of local structures and atomic packing on glass-forming ability in Cu_xZr_{100-x} metallic glasses." <u>Applied Physics Letters.</u> 96 (2010), 021901.
18. Wessels, V., A.K. Gangopadhyay, *et al*. "Rapid chemical and topological ordering in supercooled liquid $Cu_{46}Zr_{54}$." <u>Physical Review B.</u> 83 (2011), 094116.
19. Cheng, Y.Q., H.W. Sheng, E. Ma. "Relationship between structure, dynamics, and mechanical properties in metallic glass-forming alloys." <u>Physical Review B.</u> 014207 (2008), 014207.
20. Jalali, P., M. Li. "Atomic size effect on critical cooling rate and glass formation." <u>Physical Review B.</u> 71 (2005), 014206.

21. Kokotin, V., H. Hermann. "Computational analysis of the atomic size effect in bulk metallic glasses and their liquid precursors." Acta Materialia. 56 (2008), 5058-5065.
22. Kokotin, V., H. Hermann. "Geometrical aspects of the glass-forming ability of dense binary hard-sphere mixtures." Scripta Materialia. 61 (2009), 261-264.
23. Lee, H.J., T. Cagin, W.L. Johnson, W.A. Goddard. "Criteria for the formation of metallic glasses: The role of atomic size ratio." Journal of Chemical Physics. 119 (2003), 9858-9870.
24. Sha, Z.D., Y.P. Feng, Y. Li. "Statistical composition-structure-property correlation and glass-forming ability based on the full icosahedra in Cu-Zr metallic glasses." Applied Physics Letters. 96 (2010), 061903.
25. Grosse, S., G. Orveillon, O.N. Senkov, D.B. Miracle. "Thermodynamic analysis of glass-forming ability in a Cu-Mg-Zn ternary alloy system." Physical Review B. 73 (2006), 224202.
26. Kim, D., B-J Lww, N. Kim. "Prediction of composition by dependency of glass forming ability of Mg-Cu-Y alloys by thermodynamics approach." Scripta Materialia. 52 (2005), 969-972.
27. Yang, B.J., J.H. Yao, et al. "Al-rich bulk metallic glasses with plasticity and ultrahigh specific strength." Scripta Materialia. 61 (2009), 423-426.
28. Miracle, D. B. "Partial Coordination Numbers in Metallic Glasses and Insights into Atomic Bonding and Packing Efficiency." Ohio State, Columbus. 26 Jan. 2011. Lecture.
29. Ge, L., X. Hui, E.R Wang, et al. "Prediction of the glass-forming ability in Cu-Zr binary and Cu-Zr-Ti ternary alloys." Intermetallics. 16 (2008), 27-33.
30. "Molecular Dynamics." Wikipedia. <http://en.wikipedia.org/wiki/Molecular_dynamics>. Accessed on 19 May 2011.
31. Morris, J., U. Dahlborg, M. Calvo-Dahlborg. "Recent developments and the outstanding challenges in theory and modeling of liquid metals." Journal of Non-Crystalline Solids. 353 (2007), 3444-3453.
32. Mendelev, M.I., M.J. Kramer, et al. "Development of suitable interatomic potentials for simulation of liquid and amorphous Cu-Zr alloys." Philosophical Magazine. 89 (2009), 967-987.
33. Zhou, X.W., H.N.G. Wadley, et al. "Atomic scale structure of sputtered metal multilayers." Acta Materialia. 49 (2001), 4005-4015.
34. Sun, M., Y. Sun, A. Wang, et al. "The effect of atom mismatch on the fragility of supercooled Lennard-Jones binary mixtures." Journal of Physics: Condensed Matter. 18 (2006), 10889-10898.
35. Daivis, P., D. Evans. "Comparison of constant pressure and constant volume non-equilibirum
36. Russew, K, L Stojanova, et al. "Thermal behavior and melt fragility number of $Cu_{100-x}Zr_x$ glassy alloys in terms of crystallization and viscous flow." Journal of Physics: Conference Series. 144 (2009), 012094.
37. Mattern, N., A. Schöps, U. Kühn, et al. "Structural behavior of Cu_xZr_{100-x} metallic glass (x = 35-70)." Journal of Non-Crystalline Solids. 354 (2008), 1054-1060.
38. Bordat, P., F. Affouard, M. Descamps. "Effect of anharmonicity on the diffusion in glassforming binary Lennard-Jones systems." Journal of Non-Crystalline Solids. 353 (2007), 3924-3927.

39. Lazarev, N.P, A.S Bakai, C. Abromeit. "Molecular dynamics simulation of viscosity in supercooled liquid and glassy AgCu alloy." <u>Journal of Non-Crystalline Solids</u>. 353 (2007), 3332, 3337.

40. Chen, T., B. Smit, A.T. Bell. "Are pressure fluctuation-based equilibrium methods really worse than nonequilibrium methods for calculating viscosity?" <u>The Journal of Chemical Physics</u>. 246101 (2009), 246101.

41. Takeuchi, A., H. Kato, A. Inoue. "Vogel-Fulcher-Tammann plot for viscosity scaled with temperature interval between actual and idea glass transitions for metallic glasses in liquid and supercooled liquids states." <u>Intermetallics</u>. 18 (2010), 406-411.

42. Brostow, W., M. Chybicki, *et al*. "Voronoi polyhedra and Delaunay simplexes in the structural analysis of molecular-dynamics-simulated materials." <u>Physical Review B</u>. 57 (1998), 13448-13458.

43. Brostow, W., J-P Dessault, B.L. Fox. "Construction of Voronoi Polyhedra." <u>Journal of Computational Physics</u>. 29 (1978), 81-92.

44. Kittel, C. *Thermal Physics*. Wiley:New York. 1969.

45. Raghavan, R., P. Murali, U. Ramamurty. "Influence of Cooling Rate on the Enthalpy Relaxation and Fragility of a Metallic Glass." <u>Metallurgical and Materials Transactions A.</u> 39A (2008), 1573-1577.

46. Ohio Supercomputing Center. <http://www.osc.edu>.

47. Miracle, D.B, D.V Louzguine-Luzgin, A. Inoue. "An assessment of binary metallic glasses: Correlations between structure, glass forming ability and stability." <u>International Material Reviews</u>. 55 (2010), 218-256.

48. Cai, J., Y.Y. Ye. "Simple analytical embedded-atom-potential model including long-range force for FCC metals and their alloys." <u>Physical Review B.</u> 54 (1996), 8398.