Simulation of reduced glass transition temperature of Cu–Zr alloys by molecular dynamics

Su-Wen Kao,1 Chi-Chuan Hwang,2 and Tsung-Shune Chin1,3,a

1Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China
2Department of Engineering Sciences, National Cheng Kung University, Tainan 70101, Taiwan, Republic of China
3Department of Materials Science and Engineering, Feng Chia University, Taichung 40724, Taiwan, Republic of China

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Estimation of glass forming ability (GFA) of alloys by simulation before experimental trial and errors has long been a tempting pursuit in exploration of bulk metallic glasses. Reduced glass transition temperature ($T_{rg}$) of Cu$_x$Zr$_{100-x}$ alloys ($x$=46, 50, 62) were simulated by molecular dynamics using tight-binding potentials. Glass transition temperature ($T_g$) and melting temperature ($T_m$) of each alloy were calculated separately to obtain $T_{rg} = (T_g / T_m)$ as an indicator of GFA. It is shown that the calculated $T_g$ and $T_{rg}$ values of Cu$_x$Zr$_{100-x}$ alloys are in agreement with experimental data within 2%–8%, and 5%–11%, respectively. Simulation as such provides a possibility to preliminarily sort out alloys worthy of experimental trials. © 2009 American Institute of Physics. [DOI: 10.1063/1.3086623]

I. INTRODUCTION

The promising properties of metallic glasses, such as their high strength and resistance to corrosion have solicited considerable attention form scientific as well as technological societies in the past 2 decades. The discovery of bulk metallic glasses (BMGs), employing complicated combinations of multiple components in Ca-, Cu-, Fe-, La-, Mg-, Ni-, Y-, and Zr-based systems, has attracted tremendous attention.1–9 The BMGs developed so far were based on the four empirical rules:10,11 (1) a multicomponent system containing more than three elements, usually 4–8; (2) a large size difference in atomic radius among major elements, typically more than 12%; (3) high negative heat of mixing; and (4) an alloy located at the deep liquidus side of the off-eutectic compositions. Nevertheless, to estimate the glass forming ability (GFA) of BMGs, some criteria of GFA were used, such as reduced glass transition temperature ($T_{rg} = T_g / T_m$, where $T_g$ is the glass transition temperature, $T_m$ is the melting temperature);12 supercooled liquid region ($\Delta T = T_g - T_r$, where $T_r$ is the crystallization temperature);12 and gamma factor [$\gamma = T_g / (T_g + T_m)$],13 among others.

Nowadays, all the GFA criteria were concluded by measured data $T_g$, $T_r$, and $T_m$ from experimentally attained amorphous alloys, not beforehand. Trials to calculate properties of amorphous alloys dated back to early 1970s. Uhlmann14 calculated the time-temperature transformation curves and estimated the critical cooling rates based on the isothermal transformation kinetics and nucleation theory. In 1980s, Barandiaran and Colmenero15 and Takeuchi and Inoue16 successfully evaluated critical cooling rate by thermodynamically calculated GFA of Pd–Cu based alloys, which matches well with experimental data. Recently, molecular dynamics (MD) simulation has been widely applied to calculate amorphous alloys in terms of volumetric properties, pressure effect on crystallization behavior of amorphous alloys during isothermal annealing, diffusion behavior, and local atomic structures in nonequilibrium metals.21

Moreover, Lazarev et al.,22 Duan et al.,23 and Kazanc24 made use of MD to estimate $T_g$ of Cu$_{40}$Ag$_{60}$, Cu$_{46}$Zr$_{54}$, and Cu$_{50}$Ni$_{30}$ (Ref. 24) amorphous alloys, respectively. Holender25 and Mei et al.,26 calculated melting point of single elements Ag, Au, Cu, and Ni;25 and Al,26 respectively. Teichler,27 Han and Teichler,27 and Yang et al.28 calculated melting point of alloys Ni$_{0.33}$Zr$_{0.67}$, AuCu, AuCu$_3$, Cu$_{33}$Ni$_{67}$, and Ni$_3$Al,28 respectively. However none of them simultaneously deals with the calculation of $T_g$ and $T_m$. Thus GFA criteria were not calculated before as to the best knowledge of current authors.

In this research, we adopted tight-binding potential in MD simulation to calculate volumetric properties of Cu–Zr alloys. Through the heating to form a liquid and the quenching to form an amorphous alloy, volume variation versus temperature is obtained. The $T_m$ and $T_g$ can thus be attained by closely examining the volume changes. The value of reduced glass transition temperature, $T_{rg} = T_g / T_m$, serves as a useful indication of GFA. Hence the major purpose of this study is an intention to predict GFA explicitly through calculation.

The Cu–Zr BMGs were selected for calculation in this study for two major reasons. Cu–Zr BMGs have been extensively explored experimentally, plenty of experimental data were published for comparisons. Moreover, tight-binding potentials are available for Cu and Zr elements. Our experiences showed that MD method based on tight-binding potential performs well in treating melting and glass transition of transition metals. Compositions at around Cu$_{50}$Zr$_{50}$ were ar-
TABLE I. Tight-binding parameters (Ref. 32).

<table>
<thead>
<tr>
<th>Structure</th>
<th>( r_0 ) (Å)</th>
<th>Atomic mass</th>
<th>( A ) (eV)</th>
<th>( \xi ) (eV)</th>
<th>( p )</th>
<th>( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu fcc</td>
<td>2.56</td>
<td>63.546</td>
<td>0.0855</td>
<td>1.224</td>
<td>10.96</td>
<td>2.278</td>
</tr>
<tr>
<td>Zr hcp</td>
<td>3.20</td>
<td>91.224</td>
<td>0.1934</td>
<td>2.2792</td>
<td>8.25</td>
<td>2.249</td>
</tr>
</tbody>
</table>

\( r_0 \) indicates the atomic diameter of each element.

II. SIMULATION METHODS

MD simulation is a powerful tool in materials research, and has been used to provide an atomic description of the crystallization and glass forming processes during rapid solidification of alloys. The many-body, tight-binding potential model is utilized to represent the interatomic forces existing between atoms in MD simulation. Tight-binding MD is the second moment approximation of the tight-binding scheme, and was proposed by Tomanek et al. \(^{31}\) It is based on a small set of adjustable parameters, and at least in principle, is suitable for extension to high moments of electronic density of states. Based on this model, \(^{32}\) the energy of a single atom can be divided into two parts, those of attractive and repulsive components. The attractive potential \( E_A \) is given by

\[
E_A = -\sum \frac{\xi_{ab}^2 \exp\left(-2q_{ab}\left(\frac{r_{ij}}{r_0^a} - 1\right)\right)}{1},
\]

where \( r_{ij} \) represents the distance between atoms \( i \) and \( j \), \( r_0 \) is the first-neighbor distance, \( \xi \) is an effective hopping integral and \( q \) describes its dependence on the relative interatomic distance, and \( \alpha \) and \( \beta \) are the different lattices of unlike neighboring atoms. Both \( q_{ab} \) and \( \xi_{ab} \) are the geometrical average of those in \( \alpha \) and \( \beta \) lattices.

The repulsive interaction term is normally assumed to be pairwise, and described by a sum of Born–Mayer ion-ion repulsions

\[
E_R = \sum A_{ab} \exp\left[-p_{ab}\left(\frac{r_{ij}}{r_0^a} - 1\right)\right].
\]

The parameter, \( p \), is related to the compressibility of the bulk metal. \( A \) is dependent on the experimental values of the lattice parameter. The four parameters \( (\xi, A, p, \text{and } q) \) are fitted to know bulk properties of the crystals, such as the experimental values of cohesive energy, lattice parameter, bulk modulus, and elastic constants.

The related parameters of studied elements are shown in Table I. According to these parameters, all possible combinations that the elements of the system can have are considered, and then the geometric mean is applied for \( q_{ab} \), \( \xi_{ab} \), \( A_{ab} \), and \( p_{ab} \), whereas the arithmetic mean is applied for \( r_0^a \).

The total cohesive energy of the system is then, with the band quantum mechanics in origin, incorporating a many-body summation

\[
E_C = \sum \left( E_A^i + E_R^i \right).
\]

MD simulations of the copper-zirconium alloy system were carried out using the system consisting of 4000 atoms in a cubic unit cell with atoms packed in periodic boundary conditions (crystalline) along all three directions at constant pressure. Each time step is \( 1 \times 10^{-15} \) s during the simulation process. The cutoff distances are 10 Å. Figure 1 shows thermal history of the calculated alloy systems. The alloy system was first heated at the rate 20 K/ps (or \( 2 \times 10^{13} \) K/s) from 300 K [stage (a) in Fig. 1] to 2200 K [stage (b) in Fig. 1], which is higher than the melting temperatures of Cu and Zr \( (T_m,\text{Cu}=1356 \text{ K, } T_m,\text{Zr}=2125 \text{ K}) \). The alloys were held for 15 ps at stage (a) for better homogeneity and stability. It was then quenched at the rate 20 K/ps (or \( 2 \times 10^{13} \) K/s) to 300 K [stage (c) in Fig. 1]. This allows us to study phase transformation during heating up and cooling down. Data of volume variation and structural change can be extracted at any temperature step of concern during heating up (starting at room temperature with atoms packed in crystalline forms), and cooling down (from liquidus state). This is accomplished by direct counting the configuration of atoms (volume and relative positions/distances) at each temperature step of concern, done by the computer software.

III. RESULTS AND DISCUSSION

A. Radial distribution function

Figures 2 and 3 show the calculated radial distribution function (RDF) during heating and cooling processes of the model systems, including Cu–Zr alloys and single Cu and Zr elements, at the various thermal stages presented in Fig. 1. Here, RDF representing the real-space relative position of atoms is used for structural analysis.

The RDF patterns of single metals Cu and Zr are depicted in Fig. 2 for comparison with those of alloys. Figure 2(a) shows RDF at the initial packing state of single metals with different structures: Cu (fcc) and Zr (hcp). Crystalline states are visible through the well-defined peaks, which represent positions of the first, second, third, and nth nearest neighbor atoms. Upon heating to melting as shown in Fig. 2(b), the emergence of very broad peaks shows that the structure is highly disordered corresponding to a liquid state. Even though, the first nearest neighbor atoms are almost the
same with each of their crystalline counter part. The big difference lies in the lowered and blurred second nearest neighbors and indistinguishable third and fourth nearest neighbors. However, by rapidly cooling to 300 from 2200 K at the cooling rate 20 K/ps, as displayed in Fig. 2, a splitting of the second peak takes place. This splitting is characteristic of solid amorphous structure of metallic glasses. Besides, the third nearest neighbor and the fourth nearest neighbors become manifest as compared to those of the liquid state. In the RDF of melt-quenched metallic glass, although the first nearest neighbor locates at the same spacing with that of crystalline state, those of the second and third nearest neighbors are much far part.

FIG. 2. RDF of single metals, at (a) the initial state; (b) the molten state; (c) the melt-quenched state

FIG. 3. RDF of CuZr_{100-x}, x=46, 50, 62, at (a) the initial state before heating; (b) the molten state; (c) the melt-quenched state
Figure 3(a) shows typical RDF patterns of close-packed Cu$_x$Zr$_{100-x}$, $x=46, 50, and 62$ at room temperature, depicting crystalline state with well-defined RDF peaks up to 12 Å. Figure 3(b) shows a molten liquid state at 2200 K characteristic of very broad RDF peaks and vanishing peak height to be nearly indistinguishable at the third nearest neighbors and beyond. Figure 3(c) shows RDF patterns of melt-quenched alloy structure. Again, the subtle splitting (small dip) in the second RDF peak representing an amorphous state is distinguishable. Comparison among RDFs in Figs. 3(a) and 3(c), it is manifest that the first nearest neighbor of the crystalline structure and the amorphous structure after melt-quenching is the same 2.86 Å irrespective of $x$ values, and is a median value between atomic sizes of Cu (2.6 Å) and Zr (3.2 Å). The results of RDF calculation are reasonable and close to those disclosed in literature, thus our calculation by MD is acceptable.

B. Glass transition and melting temperatures

To further explore transition of structure in Cu–Zr amorphous alloys, variation of cell volume versus temperature of Cu–Zr alloys during heating and cooling cycles were calculated, as typically shown in Fig. 4. The heating curve starts with crystalline structure, until 2200 K, and the system is rapidly cooled down. The higher volume after cooling corresponds to more free volume of the “amorphous phase” formed as compared to that of starting crystalline state. A parameter often used as a measure of transition (to a glass or crystal) is the Wendt–Abraham (WA) parameter

$$ R = g_{\text{min}}/g_{\text{max}}, $$

where $g_{\text{min}}$ ($g_{\text{max}}$) is the value of $g(r)$ at the first minimum (maximum) in RDF curve (Fig. 2). The WA parameter lays emphasis the local character of $g(r)$ and provides a direct comparison between structures, leading to a better estimation of $T_g$. The WA transition temperature is displayed in the insets of Figs. 4(a)–4(c) for Cu–Zr alloys. The $T_g$ values estimated from WA parameters are adopted as the glass transition temperature. The calculated glass transition temperature is quite close to that reported earlier in experimental data, as shown in Table II. The deviation of calculated $T_g$ from those of experimental data is 2%–8%. Therefore, the simulated glass transition temperatures are quite believable, at least in Cu–Zr alloys of concern. In fact, Duan et al. simulated $T_g$ of Cu$_x$Zr$_{54}$ alloy using MD with Rosato–Guillope–Legrand-type many-body force-field and found that calculated value (700 K) is very close (within 0.6%) to the experimental one (696 K). We also investigated the effect of different cooling rates on glass transition temperature. Figure 5 depicts the volume versus temperature curves at three different quenching rates, 10, 15, and 20 K/ps, respectively, revealing the cooling rate dependent glass transition temperatures. The higher the cooling rate the higher the glass transition temperature, as typically shown in Fig. 4. The inset shows $g_{\text{min}}/g_{\text{max}}$ vs temperature taken from the curve of cooling rate 20 K/ps.

![Figure 4](image)

FIG. 4. (Color online) Variation of cell volume with temperature of Cu$_x$Zr$_{100-x}$, $x=46, 50, 62$ during the heating and cooling processes. The heating rate is 20 K/ps, while the cooling rates are 10, 15 and 20 K/ps, respectively. The inset shows $g_{\text{min}}/g_{\text{max}}$ vs temperature taken from the curve of cooling rate 20 K/ps.

being an indication of a viscosity change from a solid to an undercooled liquid, is not a second order phase transition and involves no latent heat of transition.

When melting occurs, the heating curve bends upward until complete melting. However, under the adopted extremely high heating rate ($2 \times 10^{13}$ K/s) complete melting
becomes quite uncertain and highly lagging behind. Hence, in this study the authors took the point where melting starts to occur as the melting temperature ($T_m$). Calculated $T_m$ values are also shown in Table II. In fact, the calculated $T_m$ is quite close to the liquid temperature found in the Cu–Zr binary phase diagram.\textsuperscript{35}

### C. Criterion of glass forming ability: The reduced glass transition temperature

$T_{rg}$ can be obtained by simply dividing $T_g$ over $T_m$. Table II is a collection of experimental data and calculated results of $T_g$, $T_m$, and $T_{rg}$ versus copper concentration in amorphous Cu–Zr alloys.

The calculated $T_{rg}$ values deviate 5%–11% from those of experimental ones, still quite reasonable. Let us closely examine the calculated $T_{rg}$ values. The highest calculated $T_{rg}$ value (0.63) occurs in Cu$_{62}$Zr$_{38}$ alloy, while the highest experimental $T_{rg}$ value occurs in Cu$_{62}$Zr$_{38}$ alloy. The reason of such a difference is due to the much higher calculated $T_m$ value (1307 K) versus experimental one (1180 K) of the Cu$_{62}$Zr$_{38}$ alloy. In fact, all these three alloys were reported to cast into the same diameter of 2 mm BMG despite of a big difference in $T_{rg}$ values (0.56–0.62), in experiments or in calculations. This is the reason why modified GFA criteria, such as the gamma factor, were proposed to better substitute $T_{rg}$. Nevertheless, $T_{rg}$ still serves as an easier evaluation measure for GFA that $T_{rg}$ value is better larger than 0.5 for BMG, and of course the larger the better. Our simulation at least shows that all the three alloys have $T_{rg}$ values larger than 0.55, which corresponds to the chance of attaining BMG, as been experimentally proved.

### IV. CONCLUSIONS

MD simulation with tight-binding potentials has been made in this work to gain reduced glass transition temperature, which is a criterion of GFA, of binary Cu–Zr alloys: Cu$_{62}$Zr$_{38}$, Cu$_{50}$Zr$_{50}$, and Cu$_{46}$Zr$_{54}$. RDF patterns, glass transition temperature ($T_g$), and melting temperature ($T_m$) were deduced from atomic positions and the change in cell volume versus temperature in the simulation. The GFA criterion, reduced glass transition temperature ($T_{rg}$) is simply deduced by dividing $T_g$ over $T_m$. The agreement in $T_g$ and $T_{rg}$ between calculated values and the experimental data in literatures are within 2%–8%, and 5%–11%, respectively. Moreover the calculated $T_{rg}$ values of the three alloys are all larger than 0.55, matching with the empirical facts of BMG formation. MD simulation thus provides a simple method to evaluate GFA of alloys whose component elements have available tight-binding potentials. This helps at least to screen promising alloy compositions worthy of further experimental trials to much lessen time consuming trials and errors.

### ACKNOWLEDGMENTS

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### TABLE II. Calculated and simulated $T_g$, $T_m$, and $T_{rg}$ values of the Cu–Zr alloys.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Experimental $T_g$ (K)</th>
<th>Experimental $T_m$ (K)</th>
<th>Simulated $T_g$ (K)</th>
<th>Simulated $T_m$ (K)</th>
<th>Simulated $T_{rg}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{62}$Zr$</em>{38}$</td>
<td>696 0.58</td>
<td>753 1200</td>
<td>0.63</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>680 0.56</td>
<td>713 1211</td>
<td>0.59</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{46}$Zr$</em>{54}$</td>
<td>732 0.62</td>
<td>722 1307</td>
<td>0.55</td>
<td>26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 5. Variation in glass transition temperatures with different cooling rates, 10, 15, and 20 K/ps, respectively