Factors influencing deformation stability of binary glasses

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A possible mechanism of strain accommodation in large deformation of glasses is crystallization; deformation stability is a measure of the resistance of glasses to crystallization. We study the effect of atomic size ratio and atomic stiffness parameter (related to the curvature of the interatomic potential) on deformation stability of binary glasses using molecular static simulations. The deformation stability of a glass is found to increase with increasing atomic size ratio and magnitude of the atomic stiffness, which is proportional to the bulk modulus of the pure crystalline system, as well as the ratio of atomic stiffnesses of constituent atoms. To understand the role of the above parameters on deformation stability, misfit energies of randomly substituted solid solution fcc crystals and glasses are compared for various atomic size ratios and atomic stiffness values. Unlike in fcc solid solution, the misfit energy of binary glasses is found to be insensitive to the atomic size ratio. It is also found that the packing fraction of glasses is insensitive to the atomic size ratio, consistent with the above result. Beyond a critical atomic size ratio, the misfit energy of fcc solid solution exceeds the energy of the glass, thus making the amorphous state completely stable to deformation induced crystallization. Our analysis shows that critical atomic size ratio decreases with increasing atomic stiffness which leads to an increase in the deformation stability of glasses. © 2008 American Institute of Physics. [DOI: 10.1063/1.2839300]

I. INTRODUCTION

Many experiments suggest that metallic glasses crystallize during deformation.1–9 Deformation induced crystallization of glasses is also observed in atomistic simulations.10–12 Deformation induced crystallization is a possible mechanism for large scale strain accommodation in glasses, and a possible cause for the high toughness of metallic glasses.13 In an earlier work,12 we have studied deformation induced crystallization using atomistic simulations to identify the microscopic parameters (such as “potential energy barrier”) that control crystallization of glasses. The propensity of the glasses to crystallize during the deformation is seen to decrease with the increase of the energy barrier for the atoms to “cross” each other. While the above study and the other simulations reported in the literature (Lee et al.10 and Tarumi et al.11) on deformation induced crystallization of glasses are conducted on monoatomic glasses, many other factors, viz., atomic size ratio, composition, enthalpy of mixing, etc., become important in multicomponent glasses. Many of these factors are known to influence the glass forming ability/thermal stability of metallic glasses.14–17 It is therefore natural that these parameters also influence the deformation stability which is the resistance of a glass to deformation induced crystallization.

Of the factors influencing glass forming ability, atomic size ratio is suggested to be a key parameter.18 Based on his efficient cluster packing model, Miracle19–21 showed that certain atomic size ratios are preferred in all bulk glass forming alloys. His model could predict the compositions of many of the existing bulk metallic glasses. Egami22,23 proposed a topological instability criteria for explaining the role of atomic size ratio on glass formability. One of the three empirical rules for bulk glass formation, as formulated by Inoue,17 is that the minimum atomic size difference of the constituents be greater than 12%. Lee et al.24 performed molecular dynamics simulations to investigate the phases that result from rapid solidification of binary alloys as a function of various atomic size ratios. Jalali and Li25 conducted molecular dynamics simulations on binary hardsphere mixtures allowing them to rapidly solidify at high rates of cooling, and obtained the critical cooling rate for glass formation as a function of atomic size ratio and composition. In addition to the geometric parameter such as the atomic size ratio, the “atomic stiffness” of the constituent atoms plays a crucial role. Atomic stiffness is related to the curvature of the interatomic potential at the equilibrium separation distance and controls the stiffness properties such as the bulk modulus of the materials. Ramachandrarao26 studied the role of the bulk moduli of the constituent atoms on the glass forming ability and the easy glass forming composition. While there is a substantial amount of literature that investigates the role of the geometric parameter such as the size ratio, the role of atomic stiffness parameter on stability of glasses has not received much attention.

With regard to deformation stability, the influences of parameters such as atomic size ratio, the magnitude of the atomic stiffness, the atomic stiffness ratio, and composition...
have not been hitherto investigated. This work is undertaken with the objective of understanding how these parameters control deformation stability of binary glasses. We address this issue via atomistic simulations with model potentials constructed to control the parameters listed above. We find that the atomic size ratio has the expected effect on deformation stability, i.e., very different atomic sizes render the glass stable to deformation induced crystallization. Further, we find that the magnitude of the atomic stiffness and the ratio of atomic stiffness of the two constituents, which is proportional to the ratio of the bulk modulus of the pure crystalline systems, also play a crucial role as discussed below in the paper. “Stiffer” atoms provide for glasses with better deformation stability. Similarly, a large stiffness ratio also contributes to the resistance of the glass to deformation induced crystallization.

This paper is organized as follows. In the next section, we outline the simulation method and the details of the potential model. Results are given in Sec. III followed by a discussion in Sec. IV. The paper is concluded in Sec. V.

II. SIMULATION DETAILS

The system we study is a binary mixture of particles A and B which interact through a Lennard–Jones-type potential of the form

\[ V_{\alpha\beta}(r) = \frac{P_{\alpha\beta}}{r^m} - \frac{Q_{\alpha\beta}}{r^6} + R_{\alpha\beta}, \]

where \( \alpha \) and \( \beta \) represent the species of interacting atoms; \( P_{\alpha\beta}, Q_{\alpha\beta}, R_{\alpha\beta}, \) and \( m \) are parameters. The parameters are chosen to obtain the desired equilibrium separation distance \( r_0^{\alpha\beta} = (m P_{\alpha\beta} / 6 Q_{\alpha\beta})^{1/(m-6)} \), potential energy depth \( V_{\alpha\beta}(r_0^{\alpha\beta}) \), and the curvature of potential \( V_{\alpha\beta}(r_{0}^{\alpha\beta}) \). We choose \( \sigma, \epsilon, \) and \( m_0 \) as the reduced units for length, energy, and mass, respectively, where \( \sigma = (P_{AA}/Q_{AA})^{1/(m-6)}, \epsilon = (Q_{AA}/4) \times (Q_{AA}/P_{AA})^{1/(m-6)}, \) and \( m_0 = 1.0 \). The unit of time is \( t_0 = \sigma \sqrt{m_0 / \epsilon} \). Temperature is expressed in \( \epsilon / k \), where \( k = 1.0 \) in reduced units. The sizes of the atoms A and B are proportional to the \( r_0^{AA} \) and \( r_0^{BB} \), respectively. The ratio \( r_0^{BB} / r_0^{AA} \) characterizes the atomic size ratio \( \lambda \). The potential energy depth \( V_{\alpha\beta}(r_0^{\alpha\beta}) \) is maintained constant for all of potentials so as to eliminate the mixing enthalpy effects. Atomic stiffness \( S_{\alpha\beta}^{AA}(r_{0}^{\alpha\beta}) \), is defined by the curvature of the potential at \( r_0 \). \( S_{\alpha\beta}^{AA} \) determines the bulk modulus of a crystalline solid made of only A atoms. The ratio of the curvatures \( S_{\beta\beta}^{BB}/S_{\alpha\alpha}^{AA} \) is the atomic stiffness ratio \( \alpha \). Two different cases are studied. In the first case, \( S_{\alpha\alpha}^{AA} \) and \( S_{\beta\beta}^{BB} \) are increased proportionally by incrementing \( m \) (i.e., \( \alpha \) is constant \( = 1.0 \) [see Fig. 1(a)], and in the second case, \( S_{\alpha\alpha}^{AA} \) is maintained constant and \( \alpha \) is varied [see Fig. 1(b)]. This is done so as to understand the effect of the absolute value of the atomic stiffness and the ratio of the two atomic stiffnesses. The calculated values of \( S_{\alpha\alpha}^{AA} \) for \( m = 8, 12, \) and 16 are 42.0, 62.0, and 82.0, respectively.

The glasses used in the simulations are prepared by the following steps. (1) A randomly substituted solid solution of fcc lattice (12 \( \times \) 12 \( \times \) 8, 4608 atoms) with the chosen composition \( x \) (fraction of \( B \) atoms), is created. (2) The alloy is equilibrated at a temperature of 2.5\( \epsilon / k \) (where melting point, \( T_m = 2.0 \epsilon / k \)) for 50\( t_0 \) and slowly cooled to 0.001\( \epsilon / k \) for 150\( t_0 \) at constant zero pressure. (3) A quench to zero temperature is done by minimizing the energy. Periodic boundary conditions are applied in all the directions during the melting and quenching simulations.

For the deformation simulations the glasses are prepared by choosing \( \lambda \in \{1.03, 1.06, 1.09, 1.12\}, \ x \in \{0.10, 0.25, 0.50\}, \ \alpha \in \{1.0, 1.5, 2.0\}, \) and \( m \in \{8, 12, 16\} \). The glass samples are subjected to uniform deformation such that \( \epsilon_{11} = \gamma / 2, \epsilon_{22} = -\gamma / 2, \) and \( \epsilon_{33} = 0, \) where \( \epsilon_{11}, \epsilon_{22}, \) and \( \epsilon_{33} \) are the nonzero strain components (all other components are zero). The state of strain is chosen such that the sample is subjected to a shear strain of \( \gamma \) at 45° to the 1 and 2 axes. The deformation is accomplished by incrementally applying the \( \gamma \) of 0.01\% at each step up to \( \gamma_{\text{max}} = 65.0\% \) (details may be found in Ref. 12). At each step the atomic positions and the box dimensions are rescaled appropriately and the energy is minimized using conjugate gradient method. This simulates large deformation of the glass at zero temperature.
III. RESULTS

Fifty glass samples are prepared for each combination of atomic size ratio \( \lambda \), composition \( x \), atomic stiffness \( S^{A4} \), and stiffness ratio \( \alpha \), which are subjected to shear deformation.

In each case a fraction of the samples are found to crystallize while the rest of them remain amorphous throughout the deformation up to a maximum shear strain of 65%. The fraction of crystallized samples, \( f_c \), measures the propensity of the glass to undergo deformation induced crystallization. A value of \( f_c = 1.0 \) indicates poor deformation stability, while \( f_c = 0.0 \) indicates high deformation stability.

The results of the simulations showing \( f_c \) for various glasses as a function of \( \lambda, x \), and \( S^{A4} \) (\( \alpha = 1.0 \)) are presented in Table I. We observe that \( f_c = 1.0 \) for the glass belonging to \( \lambda = 1.03, x = 0.1 \). Since \( \lambda \) is close to unity, which is the case of single component glasses, these glasses are highly prone to crystallization. The deformation stability for these glasses \( (\lambda = 1.03, x = 0.1) \) can be characterized using critical shear strain \( \gamma_c \), which is the average strain at which crystallization occurs in the deformation process. We observe an average \( \gamma_c \approx 30\% \) in single component glasses.\(^{12}\) As is evident the size ratio has a very strong influence on the deformation stability. With increasing solute concentration \( x \) (for \( \lambda = 1.03 \) and \( m \approx 12 \)) we observe a drop in \( f_c \). For glasses with large atomic size differences \( (\lambda = 1.12 \) and \( x = 0.5) \), \( f_c = 0.0 \) indicating high deformation stability in these glasses. To study the effect of the magnitude of the atomic stiffness (related to the bulk modulus of the system), calculations were done by varying \( S^{A4} \) (while keeping the stiffness ratio \( \alpha = 1.0 \)).

As is evident from Table I, a larger value of the atomic stiffness stabilizes the glass against deformation induced crystallization. Further, we studied systems where the atomic stiffnesses of the two species were different (keeping all other parameters fixed), i.e., for values of \( \alpha \neq 1 \), the results of which are shown in Table II. Clearly, system containing atomic constituents with different atomic stiffnesses resists deformation induced crystallization.

The principal results of our atomistic simulation study are the following:

1. Monoatomic systems are more prone to deformation induced crystallization. In our calculations we find that increasing solute concentration \( x \) increases deformation stability.
2. Glasses made of constituents with different atomic sizes (\( \lambda \neq 1 \)) have larger deformation stability.
3. Deformation stability increases with increasing magnitude of atomic stiffness \( S \) of all the constituent atoms.
4. The ratio of atomic stiffness \( \alpha \) also play a crucial role; systems with \( \alpha \neq 1 \) are more stable to deformation induced crystallization.

IV. DISCUSSION

We now investigate the physical origins of the above results with further calculations and comparisons with previous work. The energy of a configuration of atom, be it in the amorphous or the crystalline (solid solution) state, is determined by the four parameters \( (\alpha, x, S, \lambda) \) discussed above. In the cases where the energy of the glass \( U_G \) is lower than that of the solid solution crystal \( (U_X) \), the glasses will not undergo deformation induced crystallization. On the other hand, if \( U_X < U_G \), the glass is in a metastable state and its propensity to crystallization is determined by the energy barriers that separate the glassy minimum from the crystalline minimum. Note that the present study is focused on quasi-static deformation at zero temperature. The movement of atoms to cross the energy barriers is brought about by the deformation induced stresses generated during the deformation as opposed to thermal activation. The free volume distributed randomly among the atoms plays the role of “thermal fluctuations.” While the thermal fluctuations of atoms contribute to the atomic rearrangement process at finite temperatures, the overall trends as observed from stress-driven zero temperature simulations are useful in understanding the intrinsic resistance of glasses to deformation induced crystallization.

In the binary systems, the most important contribution to the total energy of the system is from the “misfit energy” that arises from size differences of the atoms. An estimate of the misfit energy in the solid solution crystalline state can be obtained, following arguments similar to those of Ramachandrarao.\(^{26}\)
function of atomic size ratio and for two compositions. Interestingly, the energy is insensitive to the atomic size ratio, in stark contrast with the solid solution crystalline state. The physics of this result may be understood by noting that in atomistic calculation all the bond energies are identical (since stiffness ratio is unity), and hence the most important contribution arises from the misfit energy. The role of structure in determining the misfit energy may be understood via a schematic diagram shown in Fig. 3. In random solid solution binary crystals the bond lengths are constrained which results in “compressive stresses” on larger atoms and “tensile stresses” on smaller atoms, whereas in glasses such constraints are not operative. This argument can be further corroborated by a study of the atomic level stresses in glasses and solid solution crystals. The distributions of local atomic pressure, $p_i = (1/\nu) \sum F_{ij} r_{ij}$ (where $F_{ij}$ is the force between two particles, $i$ and $j$, separated by a distance $r_{ij}$), calculated for various binary fcc solid solutions and glasses are shown in the Fig. 4. In binary solid solution crystal, the larger atoms experience “compression,” while smaller atoms undergo “dilation,” which correspond to the two distinct peaks in the pressure distribution. The separation between the peaks increases with increasing size ratio $\lambda$, increasing the misfit energy. In glasses there is a single broad peak, which remains unchanged with atomic size ratio $\lambda$ and composition $x$, providing insights for the origin of the insensitivity of the energy on $\lambda$ and $x$. Our results are also consistent with the topological theory of Egami and Waseda, which elucidates the role of atomic size ratio on glass formability. Ac-
TABLE III. Dependence of critical atomic size ratio $\lambda_c$ on atomic stiffness.

<table>
<thead>
<tr>
<th>m</th>
<th>$\lambda^{14}$</th>
<th>$\alpha$</th>
<th>$\lambda_c (x=0.50)$</th>
<th>$\lambda_c (x=0.10)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>41.8</td>
<td>1.0</td>
<td>1.19</td>
<td>1.27</td>
</tr>
<tr>
<td>12</td>
<td>61.6</td>
<td>1.0</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>16</td>
<td>82.2</td>
<td>1.0</td>
<td>1.17</td>
<td>1.23</td>
</tr>
<tr>
<td>8</td>
<td>59.8</td>
<td>1.0</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>12</td>
<td>59.8</td>
<td>1.5</td>
<td>1.17</td>
<td>1.24</td>
</tr>
<tr>
<td>12</td>
<td>59.8</td>
<td>2.0</td>
<td>1.17</td>
<td>1.23</td>
</tr>
</tbody>
</table>

where $d$ is the diameter of the $A$ atom (calculated from the equilibrium lattice parameter of the single component system) and $\rho$ is the number density obtained from atomistic calculations. The results are shown in Fig. 2(b). Interestingly, we see that the packing fraction of the glass is insensitive to the atomic size ratio. However, the solid solution fcc crystal shows dramatic decrease of the packing fraction when the atomic size ratio changes from unity. Indeed, the packing fraction of the fcc solid solution crystal falls below that of the glass at a critical atomic size ratio, which is very close to the corresponding critical atomic size ratio obtained by a study of the energy. Moreover, we uncover an interesting empirical correlation: $U \propto -\phi^3$. The quantity $1 - \phi$ is indeed proportional to free volume, and many experiments of metallic glasses have already shown that the enthalpy change measured by differential calorimetry is proportional to the free volume and is consistent with our simulation results. The enthalpy change is routinely used for measuring free volume in experiments. This result also suggests the equivalence between energy and packing fraction criteria in bulk metallic glass formation. Indeed, Miracle’s model of bulk metallic glasses is based on the maximum packing of constituent atoms.

The result of the insensitivity of the packing fraction of the glass on the atomic size ratio is consistent with the calculations of Jalali and Li on hard sphere systems. They have suggested that when the packing fraction of a binary crystals falls below that of a glass, crystalline state is no more stable and glassy state is preferred. Our study indicates the energetic origin of this criterion, since the critical size ratio at which the energy of the glassy state becomes lower than that of the crystal is essentially the same as that at which the packing fraction of the crystal falls below that of the glass. Clearly, Jalali–Li criterion is also applicable to non-hard sphere systems and, in particular, for the deformation stability of glasses. Glasses whose packing fractions are larger than those of the corresponding solid solution crystal will be stable to large shear deformation.

It is interesting to note that Kawasaki et al. studied the two dimensional polydisperse Lennard–Jones-type glasses and observed a correlation between medium range crystalline order and dynamic heterogeneity. We have checked if there is any similar order in the as-prepared glasses before shearing but did not find any apparent medium range order that can be correlated with the deformation induced crystallization. The correlation between the deformation induced crystalization and dynamic heterogeneity can be an important future direction in further understanding of the stability of glasses.

V. CONCLUSIONS

We have investigated the deformation stability of binary glasses using molecular static simulations. We studied the influence of various parameters such as composition, size ratio, magnitude of atomic stiffness, and atomic stiffness ratio. We found that a large difference in atomic sizes/atomic stiffness ratio play a crucial role in determining the deformation stability.

Another quantity of interest is the packing fraction $\phi$, which is calculated using

$$
\phi = \frac{\pi d^3 \rho}{6(1 - x + x \lambda^3)},
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where $d$ is the diameter of the $A$ atom (calculated from the equilibrium lattice parameter of the single component system) and $\rho$ is the number density obtained from atomistic calculations. The results are shown in Fig. 2(b). Interestingly, we see that the packing fraction of the glass is insensitive to the atomic size ratio. However, the solid solution fcc crystal shows dramatic decrease of the packing fraction when the atomic size ratio changes from unity. Indeed, the packing fraction of the fcc solid solution crystal falls below that of the glass at a critical atomic size ratio, which is very close to the corresponding critical atomic size ratio obtained by a study of the energy. Moreover, we uncover an interesting empirical correlation: $U \propto -\phi^3$. The quantity $1 - \phi$ is indeed proportional to free volume, and many experiments of metallic glasses have already shown that the enthalpy change measured by differential calorimetry is proportional to the free volume and is consistent with our simulation results. The enthalpy change is routinely used for measuring free volume in experiments. This result also suggests the equivalence between energy and packing fraction criteria in bulk metallic glass formation. Indeed, Miracle’s model of bulk metallic glasses is based on the maximum packing of constituent atoms.

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stiffness provides for deformation stability. Similarly, larger magnitude atomic stiffness also provides for resistance to deformation induced crystallization. We have also obtained results for critical atomic size ratios; for system with size ratios beyond the critical value, the glasses are completely stable to deformation induced crystallization.

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