

Molecular dynamics simulations of supercooled liquid metals and glasses

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Abstract

The thermodynamic, transport and structural properties of a binary metallic glass former in solid, liquid, and glass phases were studied using molecular dynamics simulation. We used a model binary alloy system with a sufficient atomic size mismatch and observed a glass transition in a quenching process. The diffusivity and viscosity were calculated in the liquid state and the super-cooled liquid state. The smaller atom showed higher diffusivity and more configurational randomness compared to the larger atom. The viscosity increased abruptly around the glass transition temperature. The solvent/solute concentration effect on the glass transition was examined in terms of a packing fraction. We find that the glass forming ability increases with the packing fraction in the liquid state because the densely-packed material requires more time to rearrange and crystallize.

Introduction

In understanding the physics of the glass transition of metallic alloys, Molecular Dynamics (MD) simulations can provide important insights by allowing one to determine quantities which are difficult to access in real experiments or hard to obtain with reasonable precision. To precisely describe the interactions in metals and metallic alloy system, we adopted the empirical many body potential developed by Sutton and Chen [1]. Force-field parameters were optimized for face centered cubic (FCC) transition metals by fitting to such experimental properties as density, cohesive energy, moduli, and phonon frequencies [2,3].

It has been previously established that the atomic size mismatch plays a major role in the glass transition [4,5]. Therefore, the generalized binary alloy system with sufficient atomic size mismatch was chosen as a model glass former. Among possible candidates, we used Cu as the base material. For the second component, we introduced an artificial Cu-like atom, Cu^{*}, which has same force-field parameters except its size parameter, i.e. its atomic radius. By introducing Cu^{*}, we could characterize the atomic size mismatch effect on the glass transition more easily without considering other factors such as a mismatch in chemical bonding character. The atomic size ratio of Cu^{*} and Cu was set 1.13, corresponding to the Ag-Cu alloy system which is known to be a good glass former.

The simulation was performed at constant temperature, constant thermodynamic tension (TtN) MD conditions [6]. The TtN MD was started from an FCC random solid

solution with 500 atoms in a simulation cell subject to periodic boundary conditions. The heating experiment was carried out by increasing the temperature from 300 K to 1600 K in 100 K increments. After the system has reached the equilibrium liquid state, we quenched the system from 1600 K to 300 K in 100 K decrements and observed a glass transition.

Using the cooling rate of 4×10^{12} K/s, we found that the $\text{Cu}_{50}^* \text{Cu}_{50}$ alloy exhibited a glass transition around $T = 500$ K. In contrast, the pure Cu system crystallized around $T = 650$ K and formed a FCC structured crystal. Below, we present the studies on the thermodynamic, transport and structural properties of the glass forming $\text{Cu}_{50}^* \text{Cu}_{50}$ alloy.

Results and Discussion

Figure 1 shows the molar volume as a function of temperature. A sudden increase in volume is due to first-order transition such as melting or crystallization. The melting temperature of pure Cu was about 1350K, which is comparable to the experimental value of 1356K. The melting temperature of $\text{Cu}_{50}^* \text{Cu}_{50}$ alloy is significantly less than the melting temperature of pure Cu. This melting temperature depression is solely due to the atomic size mismatch, which induces high local stresses in the ordered structure. The system experiencing these high local stresses tends to be less stable and phase transforms at a lower temperature or small pressure changes. Generally, we found that the melting temperature decreases as the atomic size mismatch increases. This is not valid in a system above certain atomic size mismatch because smaller atoms can exist as interstitials and hence don't create large localized stress fields.

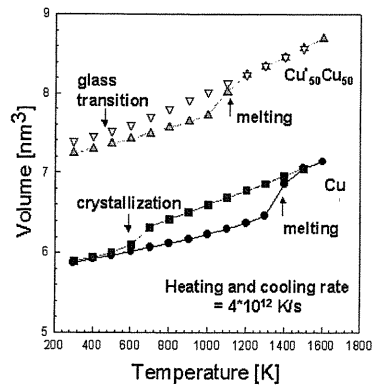


Figure 1: Volume-temperature relationship for the heating and cooling experiments of a pure Cu and model binary alloy system ($\text{Cu}_{50}^* \text{Cu}_{50}$). Note that the pure Cu show a crystallization upon cooling, but $\text{Cu}_{50}^* \text{Cu}_{50}$ vitrify and form a glass.

The diffusivity of $\text{Cu}_{50}^* \text{Cu}_{50}$ alloy was measured using Einstein relation [7]. Figure 2 shows self-diffusivities of the larger atomic species (Cu^*) and the smaller atomic species (Cu). For both species, the diffusivity showed a break from the Arrhenius type temperature dependence in the vicinity of the super-cooled liquid to glass transition temperature. The occurrence of this discontinuity in the Arrhenius behavior can be

explained by the change of a dominant diffusion mechanism from the collective motion to the atomic hopping mechanism around the glass transition temperature [8]. Using the Arrhenius type of equation, the diffusivity above the glass transition temperature can be described by

$$D = 12.4816 * \exp\left(-\frac{33.712 \text{ kJ/mol}}{RT}\right) \text{ for Cu}^*$$

$$D = 8.90306 * \exp\left(-\frac{28.941 \text{ kJ/mol}}{RT}\right) \text{ for Cu.} \quad (1)$$

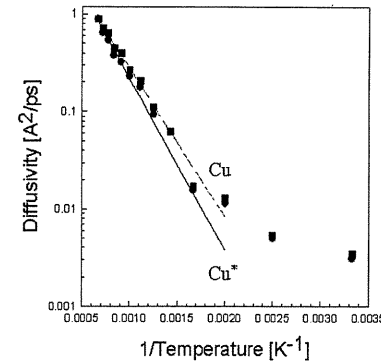


Figure 2: Self-diffusion of Cu^* and Cu in $\text{Cu}_{50}^* \text{Cu}_{50}$ alloy. The temperature dependence of diffusivity shows a break around the glass transition temperature, ($T_g = 500$ K). The temperature dependence of the diffusivity above the glass transition temperature can be described by Arrhenius relationships, Eqn. 1

The activation energy of Cu^* is greater than that of the activation energy of Cu. Furthermore, the diffusivity of Cu^* is less than the diffusivity of Cu in all temperature range, which indicates the diffusivity decreases as the atomic size increases. We think that this size dependence of diffusivity originated from configurational constraint such as the excess free volume. It should be noted that despite the size difference, all the other force-field parameters were the same in Cu^* and Cu.

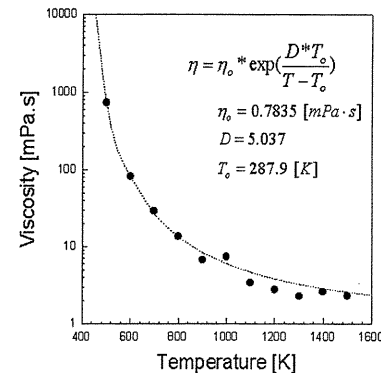


Figure 3: The temperature dependence of viscosity for a super-cooled $\text{Cu}_{50}^* \text{Cu}_{50}$ liquid. Dotted line is the Vogel-Fulcher fit and the fragility index parameter (D) shows the “fragile” liquid behavior of this binary alloy system.

The shear viscosity was calculated from the Green-Kubo relationship (by integrating the shear stress auto-correlation function) [7],

$$\eta = \frac{V}{k_B T} \int_0^{\infty} dt \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle \quad (2)$$

Figure 3 shows the viscosity data at various temperatures. The viscosity increases several orders of magnitude abruptly as the temperature approaches the glass transition temperature. Below the glass transition temperature, it was impossible to obtain a viscosity data because a pressure auto-correlation function did not converge within our simulation time scale. Above the glass transition temperature, the data was fitted by the Vogel-Fulcher equation,

$$\eta = \eta_0 * \exp\left(\frac{D * T_0}{T - T_0}\right) \quad (3)$$

The D value, often referred to as the fragility index, was 5.03519, and the VFT temperature T_0 was 287.942K, which is about 60% of the glass transition temperature. The small value of D (the fragility index) is an indication of the fragile character of this binary alloy system.

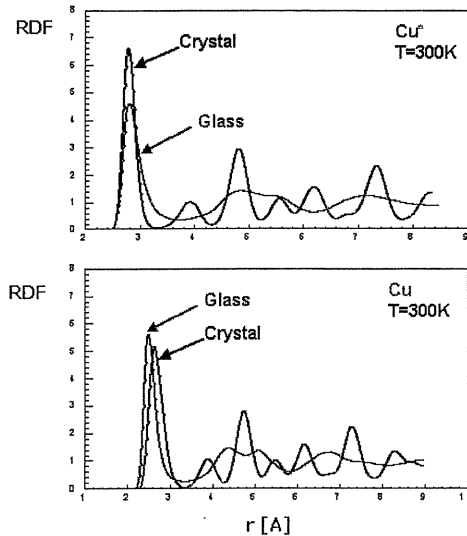


Figure 4: The comparison of radial distribution functions of Cu* and Cu in the glass state and the crystalline state. In the glass state, Cu shows more distinguishable second peak split.

In addition to the transport properties, we investigated the atomic configurational order in amorphous, crystalline, and liquid state. We used the pair distribution function to

analyze the atomic configuration. The pair distribution function provides insights into the microscopic structures. In particular, the split in the second peak indicates the structural randomness, which is a unique characteristic of an amorphous material. In Figure 4, we compared the pair distribution function of the crystalline state and the amorphous state of each atomic species separately. The shift in the first peak maximum is more prominent in the smaller atom (Cu) and also the second peak split is also more distinguishable. This result suggests that the smaller atomic species have more configurational randomness in an amorphous state compared to the larger atomic species that are less mobile. In other words, due to its higher mobility, the smaller atom explores more possible atomic configurations and freezes into an amorphous configuration as it experiences the glass transition.

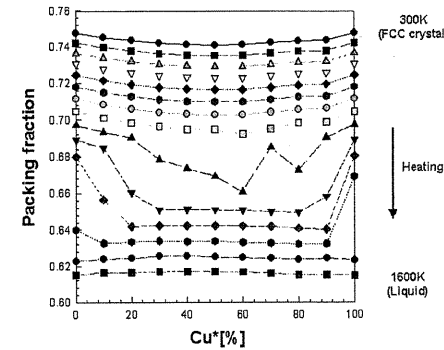


Figure 5: The packing fraction as a function of Cu concentration in heating runs. Top line corresponds to T=300 K, FCC random solid solution state, the bottom line corresponds to T=1600 K, liquid state. Each line from top to bottom represents an increase in temperature by 100 K. The curve with large packing fraction change corresponds to melting temperature. Note that the packing fraction shows a minimum at 50% concentration in crystalline state, but shows a maximum in liquid state.

Finally, we prepared a series of Cu*Cu alloys which has different solvent/solute concentration (Cu*, Cu_{100-x} with x = 0, 10, 20, ..., 100) to understand the solvent/solute concentration effect in the glass transition. We performed heating and quenching experiments for all these alloy systems. From the heating experiments, we found that the melting point shows a minimum around x = 50. Therefore, one expects that this alloy system will have a eutectic point at Cu*₅₀Cu₅₀. To relate the glass forming ability and the solvent/solute concentration effect, we introduce a packing fraction. The packing fraction is defined as the ratio of the total volume occupied by the spheres to the total volume. The highest packing fraction can be obtained in a perfect FCC or HCP crystalline state and the value corresponds to about 0.74. Because the configurational redistribution of elements of a material with a high packing fraction is relatively difficult compared to a state with a low packing fraction, the densely packed material needs more time to rearrange and crystallize [9]. Using this simple idea, we examined the relationship between the packing fraction and the glass forming ability. Interestingly, when it is random FCC crystalline state, Cu*₅₀Cu₅₀ showed a minimum packing efficiency compared to other samples, suggesting its structural instability. But when it becomes liquid states, Cu*₅₀Cu₅₀ showed a maximum packing efficiency. Indeed, samples with relatively high packing efficiency in liquid state showed glass transition, but others showed crystallization (x = 0, 10, 100).

Conclusions

The glass transition was studied in a model binary alloy ($\text{Cu}_{50}\text{Cu}_{50}$) system. The atomic size mismatch and the solute/solvent concentration are critical parameters in the glass transition. The diffusivity showed a break in the Arrhenius type of temperature dependence in the vicinity of the super-cooled liquid to glass transition temperature, which implies the change in the diffusion mechanism. The viscosity was well fitted by the Vogel-Fulcher expression. The micro-structural information was investigated using the pair distribution function. The smaller atomic species showed more structural randomness compared to the bigger atomic species. Finally, the concentration effect in the glass transition was investigated in terms of packing fraction. The glass forming ability increases with the packing fraction in the liquid state, because the redistribution of elements during the transition from amorphous state to crystal is relatively difficult in a material with high packing fraction.

Acknowledgments

This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-0080065.

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