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원자변형률을 이용한 비정질 금속의 천이온도에 관한 연구

박준영#

Study for Local Glass Transition of Bulk Metallic Glasses using Atomic Strain

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ABSTRACT

Bulk metallic glasses (BMG) have been greatly improved by the advance of synthesis process during last three decades. It was also found that the Glass Forming Ability (GFA) strongly depends on the glass transition temperature. When the temperature approaches to a critical value, the crystals nucleation from the supercooled liquid can be suppressed so that bulk glass formation possible. Egami and others found that the local glass transition temperature depends on the volumetric strain of each atom and suggested the critical transition temperature. In this paper, we explore the strain dependency of local glass transition temperature using the atomic strain defined by the deformation tensor for the Voronoi polyhedra.

Key Words : Bulk Metallic Glasses; Glass Transition; Atomic Strain

1. Introduction

Since the first synthesis of the system with amorphous phase, by rapid solidification technique, a great number of amorphous alloys have been produced for the last three decades[1]. It was reported that the critical cooling rate is inversely proportional to the reduced glass transition temperature, defined by the ratio of glass transition temperature to melting temperature, for amorphous alloys as shown in Ref. 2. Since the Glass Forming Ability is a function of glass transition temperature, it is noteworthy that the glass forming ability is studied by the view of glass transition mechanism.

There have been some approaches to analyze the glass transition by theoretical way, such as local topological instability, free volume theory and percolation concentration[3-5]. Free volume theory and percolation concentration are related with surplus space to move atoms. In contrast, Egami's approach, the

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intuitive theoretical approach, starts at the local topological instability. In this approach, the local instability is described by geometric change of the system, i.e. volume expansion as known as atom size change. This local instability is often represented by the atomic volumetric strain, instead of volume expansion. In spite of relatively unrealistic assumption like only geometric dependency and the adoption of hydrostatic pressure, the theory shows a good agreement with experiment. For instance for $Fe_{80}B_{20}$ this gives T_g=652K, which compares well with the experimental value of 660K. The objectives of this study are, first, to compare the calculated critical volumetric strain by local topological theory and the obtained critical volumetric strain from molecular dynamics simulation in the global sense, then, to present the status of atomic strains in the local view.

2. Computational Model

The $Cu_{64}Zr_{36}$ system[6,7] with 2000 atoms is chosen to obtain the amorphous structure, easily. Molecular dynamics study using Morse potential is adopted. At the first step, 1280 copper atoms and 720 zirconium atoms are randomly positioned in the cubic cell with the size of 3nm. Then, for 105steps, the cell is fully relaxed using periodic boundary condition at 300K and 1fs timestep. Finally, we obtain an amorphous structured model for glass transition. Note that the small atoms are copper and the others are zirconium. The density of the obtained model is 7.398g/cm^3, compared to the experimental value7 of 7.382g/cm^3 for $Cu_{57}Zr_{43}$. In addition, the second peak split by two, like the characteristic of amorphous materials. The first peak of Radial Distribution Function(RDF) obtained from the model shows 2.55Å for Cu-Cu, 2.85Å for Cu-Zr, 3.15Å for Zr-Zr, compared to 2.65Å for Cu-Cu, 2.80Å for Cu-Zr, 3.15Å for Zr-Zr obtained by experiments[8].

3. Theoretical Approach

3.1 Local Topological Instability

The followings are the brief introduction of Egami's theory. More details can be found elsewhere[9,10]. The main idea of this concept is that there is a critical volumetric expansion threshold beyond which the local atomic structure changes its topology. The local topology of structure can be estimated by the number of nearest neighbors, i.e. the local coordination number. The starting point of this theory is the area occupied by each atom, as known as solid angle described by radius of central atom (R_A) and embedded atoms (R_B), to calculate the coordination number. The obtained coordination number by solid angle is given by

$$N_C = \frac{4\pi\left[1-\frac{\sqrt{(3)}}{2}\right]}{\left[1-\frac{\sqrt{x(x+2)}}{x+1}\right]} \tag{1}$$

where x is the radius ratio, R_A/R_B. The volume change for topological instability is accompanied by the change of coordination number by integer. Thus, the amount of change in x that is needed to bring about the change in N_C is given by

$$\Delta x_C = \frac{1}{2} \cdot \frac{\partial x}{\partial N_C} = \frac{1}{4\pi}\frac{(x+1-\sqrt{(x(x+2)})^2\sqrt{x(x+2)}}{2-\sqrt{3}} \tag{2}$$

From this, the critical volumetric strain for local topological instability, ε_V^{crit}, is given by

$$\varepsilon_V^{crit} = \frac{3\Delta x_C}{2x} \tag{3}$$

It is noteworthy that the critical volumetric strain, ε_V^{crit}, is 0.0554, when R_A=R_B, i.e. x=1. This condition led to the expression for the glass transition temperature, T_g,

$$T_g = \frac{2\Omega K}{k_B}\left(\varepsilon_V^{crit}\right)^2 \quad (4)$$

where Ω is the atomic volume, K is the bulk modulus and k_B is Boltzmann's constant.

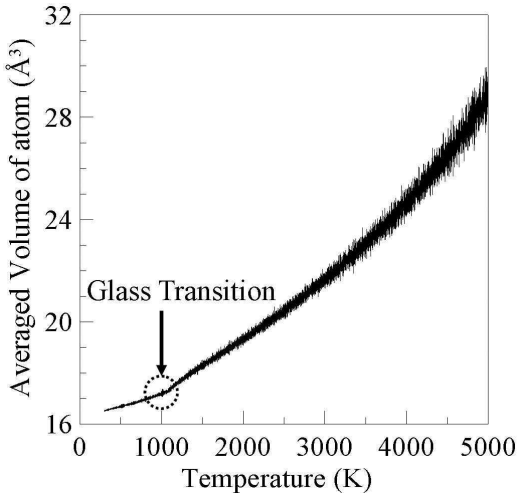


Fig. 1 The relationship between averaged volume of atom and temperature. The point with slope change is known as glass transition point[11]

4. Results and Discussion

4.1 Global view

The overall behavior at glass transition temperature is firstly reported. Fig. 1 shows the dilatation of the given model .vs. temperature. The averaged volume of each atom, i.e., total cell size divided by the number of atom is examined. As temperature goes up from 300K corresponding 16.5Å^3 of averaged atomic volume, the volume is almost linearly increased to 1100K. Then, at around 1100K, the slope of volume increase is changed as reported in other researches. The point of slope change is regarded as a proof of glass transition. And we found that this point can be reproduced by heating process and cooling process, when they are fully relaxed. After the glass transition point, the volume is monotonically increased over melting point with temperature increase.

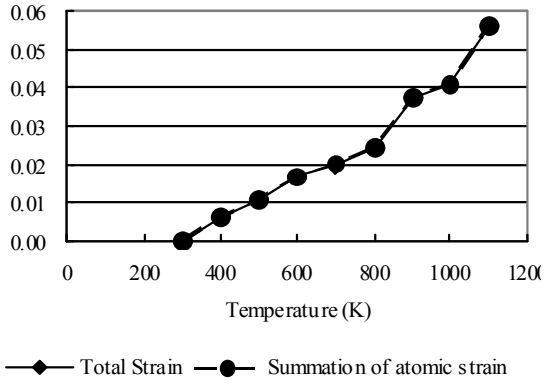


Fig. 2 The first strain invariant, K_1, measured by total cell strain and summation of atomic strain

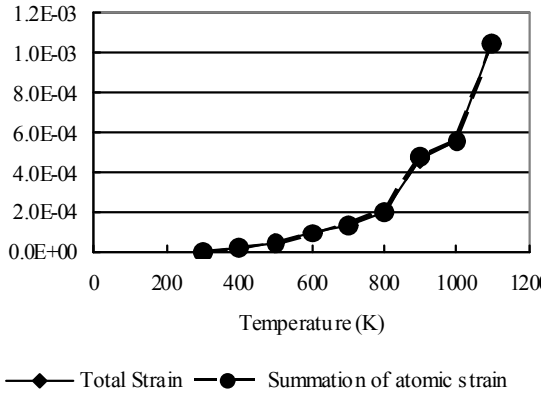


Fig. 3 The second strain invariant, K_2, measured by total cell strain and summation of atomic strain

The strain state of atoms is examined from initial state of 300K to the glass transition state of 1100K. To obtain the volumetric strain of cell and each atom, we measure the first strain invariant of whole model, K_1, as known as volumetric strain, by the developed atomic strain program. The obtained results in Fig. 2 show the almost identical curves for the total cell strain and the summation of atomic strain. The volumetric strain is also monotonically increased to 800K. Then, it makes a little bump at 900K and 1000K. At 1100K, the glass transition temperature, the

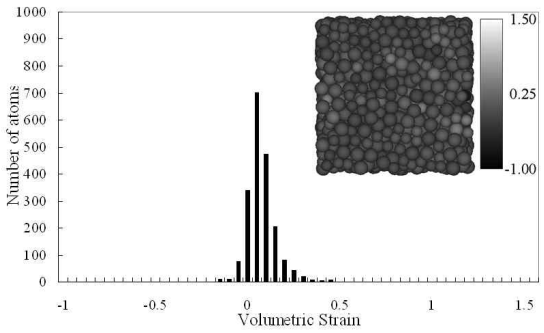
obtained strain is larger than the expected value by extrapolation of the line from 300K to 800K. In spite of the bump, there is no distinguishable thing at atomic configuration and other measurements. The value of volumetric strain corresponding to 1100K is 0.055. This is almost same with the critical volumetric strain, 0.054 suggested by Egami[10]. And the obtained temperature also coincides with the calculated temperature for copper atom surrounded by copper atoms, 1044K, by equation (4). Although there are many possibilities to make a combination of central atom and surrounded atoms by two atoms, copper and zirconium, the combination of central copper atom surrounded by pure copper atom is adopted because of the majority of copper.

The second strain invariant of whole model, K_2, is regarded as a kind of representative value of deviatic strain by the definition, while the first strain invariant, K_1 is the same with volumetric strain. The second strain invariant shows very similar shape with the first strain invariant in Fig. 3 However, K_2 is relatively quite small to be compared with K_1. It seems that the deviatic strain does not affect the glass transition, much. However, the strain invariant of each atom could be quite different[11].

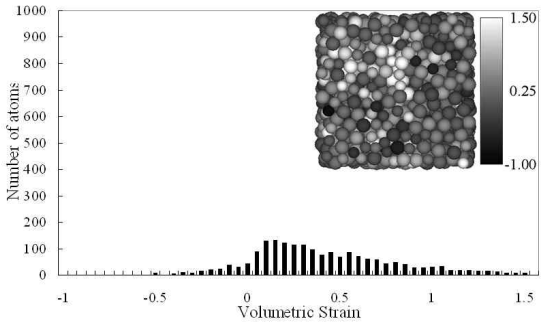
4.2 Local view

Although the overall behavior of atoms at glass transition is already checked in global view, there are still unknowns about the detail behavior in atomic view.

Fig. 4(a) and (b) depict the distribution of volumetric atomic strain, K_1, at 600K and 1100K (glass transition temperature), respectively. The atomic configuration with scale bar at the upper-right corner of each figure shows the distribution of volumetric strain of each atom, K_1. Atoms are colored according to the value of atomic volumetric strain. Black represents a strain smaller than -1.0 (volume contraction) while white represents +1.5 strain (volume expansion). As expected, the range of atomic strain



(a) K_1 at 600K



(b) K_1 at 1100K

Fig. 4 The second strain invariant, K_2, measured by total cell strain and summation of atomic strain[11]

distribution at 600K is narrow because thermal volume expansion is still small. The color of atomic configuration is also similar. However, as temperature goes up, the distribution becomes wider and flatter. For example, the largest frequency of atomic strain at 600K, 900K and 1100K are 728, 392 and 155, respectively. These correspond with the 35%, 20% and 8% of all atoms, respectively. It means that the largest frequencies are almost linearly inversed proportional to temperature increase. On the contrary, the range of atomic strain distribution becomes wider from around ±0.25 to ±1.0 as the temperature goes up to 1100K. Although the peak (the largest frequency) of distributions for each temperature is located in the range below 0.05 until 900K, the peak moves to the range from 0.05 to 0.1 at 1100K. And, the averaged atomic strain for 1100K is 0.052. This also shows a

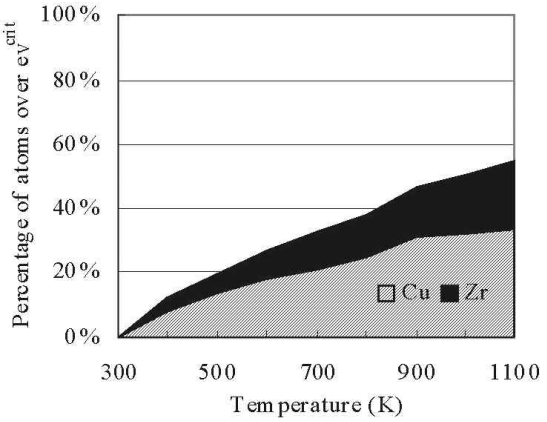


Fig. 5 The percentage of atoms over the critical volumetric strain. At glass transition temperature, the percentage reaches to around 55%

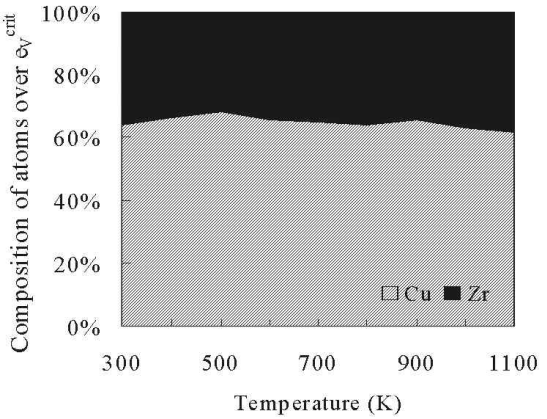


Fig. 6 The composition of atoms over the critical volumetric strain. The original composition still remains constant for the entire temperature range

reasonable agreement with the critical volumetric atomic strain, 0.054, estimated by the local topology instability theory.

The atomic configuration has almost identical color at 600K while it has variety of color at 1100K. It means all atoms have similar volumetric strain at low temperature, but the variety of strain will be wider at high temperature. It also should be noted that some atom has black color corresponding to volume contraction during thermal expansion process. It is reasonable because the local structure could be unstable even if the global structure is already stable. However, the distribution is moving to left, greater volumetric strain as temperature goes up.

Based on the agreement between theoretical value and global value, we measure the percentage of atoms over critical volumetric strain, i.e. 0.055 or 5.5% as shown at Fig. 5 where the diagonal area and black solid area are copper and zirconium, respectively. The percentage is linearly increased with temperature. It is natural because the volume is expanded with temperature increase. For example, the percentage corresponding to 400K is 12%. Then, the percentage reaches over 50% at the glass transition temperature, 1100K. It means that some of atoms already reach to the critical volumetric strain even at very low temperature. In spite of the glass transition at 1100K in the global view, the percentage reaches just 50% in the local view.

The percentage proportional to temperature has similar tendency for two atoms, copper and zirconium. Thus, the relation between temperature and the composition of atoms over the critical volumetric strain is represented in Fig. 6 The composition at 300K is the original percentage of the model, 64% of copper and 36% of zirconium. The result shows almost constant value within the entire temperature range. This means that the atoms experience homogeneous deformation regardless of atom kinds.

5. Conclusion

Using theoretical approach suggested by Egami and the atomic strain approach suggested by Mott, the glass transition process for $Cu_{64}Zr_{36}$ are analyzed. Glass transition in $Cu_{64}Zr_{36}$ occurs at 1100K corresponding to 0.55 volumetric strain in MD simulations. This result is almost identical with the results, 1044K and 0.054, computed by the Egami's theory. In the local view, the distribution of atomic strain becomes wider and flatter

as temperature goes up. The peak, i.e. the most frequent atomic strain, is moving to higher strain. The percentage of the atom over critical volumetric strain, 0.055, is proportional to temperature, regardless of atomic kinds. The percentage at glass transition is around 55%.

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