Icosahedral Order in Supercooled Liquids and Glassy Alloys

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Abstract. Formation of the icosahedral order in supercooled liquids and glassy phases is investigated for a model alloy system by using molecular dynamics simulations. The simulation results show that the short-range icosahedral order grows in the supercooled liquids as well as in the glassy phases. Structural analyses reveal that the icosahedral clusters form a network in which the clusters are connected via the pentagonal-bicap sharing. Geometrical property of the network formed by the icosahedral clusters is an origin of medium-range order in the glassy phases

Introduction

In recent years, the bulk metallic glasses [1,2] has received much scientific attention not only due to technical interest but also due to theoretical interest, since the bulk metallic system has a potential power to offer an ideal occasion to understand the physics behind the glass transition. Especially, the structural model of metallic glasses is one of the most intriguing mysteries to be solved. In satisfactory models [3,4], it is conjectured that there should be some characteristic structural unit of a short-range order (SRO) of atomic packing in glassy states, depending on the individual alloy systems. For glassy alloys with the elements of comparable atomic sizes, the characteristic unit is the icosahedral cluster, which is supported by the experimental studies [5,6]. On the other hand, it is not clear about the medium-range order (MRO), which would be formed by the spatial packing pattern of structural units or clusters. Very recently, inspired by a pioneering work [7], a promising model of MRO is proposed [8], in which the building pattern of the unit clusters is clarified in several types of metallic glasses. However, the packing morphology is so complicated especially in the alloys with high solute concentrations that there remains a mystery in the MRO formed in metallic glasses. In this context, we shall investigate the local atomic configuration in the glassy phases of a model alloy system by using the molecular dynamics (MD) simulation with paying a special attention on the formation of the icosahedral order to clarify the structural origin of the MRO in metallic glasses.

Interatomic Potentials

In the MD simulations, the atomic trajectories are calculated from the equations of motion by supposing a functional form of the interatomic potential. In this study, we employ a model alloy system, where the interaction between the elements i and j is supposed to be described by the 8-4 Lennard-Jones (LJ) potential:

$$V_{ij}(r) = e_{ij}\left\{ \left(r_{ij}/r\right)^8 - 2\left(r_{ij}/r\right)^4 \right\}, \tag{1}$$

which is proved [9] to be adequate for metallic systems. The potential has the minimum $-e_{ij}$ at the distance r_{ij}, which can be considered as the amount of chemical interaction and the atomic size, respectively. For simplicity, we consider a binary system of elements A and B with the atomic size ratio 0.8 and with equi-chemical interaction. In other words, we assume that $r_{AA} = 1$, $r_{BB} = 0.8$, $r_{AB} = (r_{AA} + r_{BB})/2 = 0.9$, and $e_{AA} = e_{BB} = e_{AB} = 1$. Then we can vary the concentration x of the solute element B. All physical quantities are expressed in the above units throughout this paper.

Simulation Methods

We consider a system containing 4000 atoms under a periodic boundary condition. The equilibrium melting temperature of a monatomic system of the element A or B is around 0.55 in the above-mentioned units. As starting liquid phases, we first prepare binary mixtures at $T = 0.7$. We then simulate rapid solidification processes or isothermal annealing processes by controlling the temperature and the pressure of the simulation system. The temperature of the system is controlled by scaling the atomic momenta and the pressure of the system is kept zero by using the constant-pressure scheme [10]. Here we should make a note about the typical order of time scale handled in this MD study. Supposed that the LJ units are identified with a typical mass, atomic radius, and melting point of metallic elements, then the unit of time becomes around 4×10^{-13} s and that of cooling rate becomes around 5×10^{15} K/s.

Growth of Icosahedral Order in Rapid Solidification

Figure 1 shows the change of the atomic volume of the $A_{40}B_{60}$ system during rapid cooling processes from a liquid phase with two different cooling rate 2×10^{-3} (rapid) and 2×10^{-4} (slow). The discontinuity around $T = 0.3$ in the slope of the temperature dependence of the volume corresponds to a liquid-to-glass transition temperature T_g, which depends on the cooling rate as marked in the figure. The glassy nature of the solidified phase is confirmed by calculating the radial distribution and by analyzing the atomic configuration [11].

In the systems where the atomic size difference between the constituent elements is small, the icosahedral clusters are the most probable candidates for a structural unit in the glassy phases. Therefore, we shall investigate the local atomic structure with paying a special attention to the icosahedral symmetry. By using
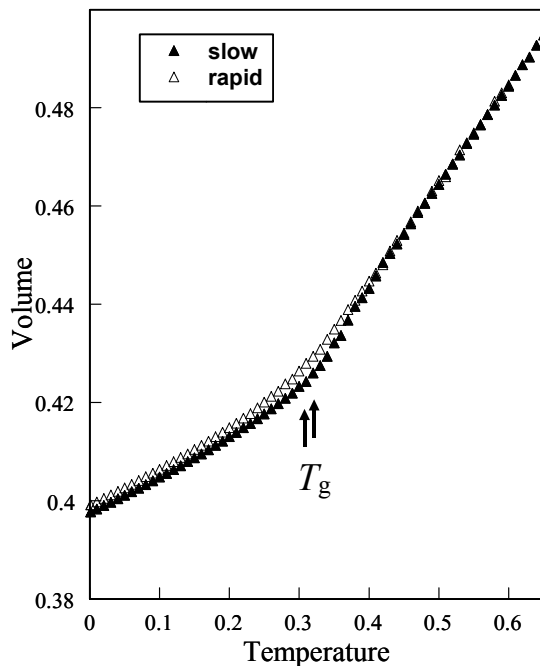

Fig. 1 Time evolution of the atomic volume of the $A_{40}B_{60}$ system in rapid solidification processes with two different cooling rates 2×10^{-3} (open triangles) and 2×10^{-4} (closed triangles).
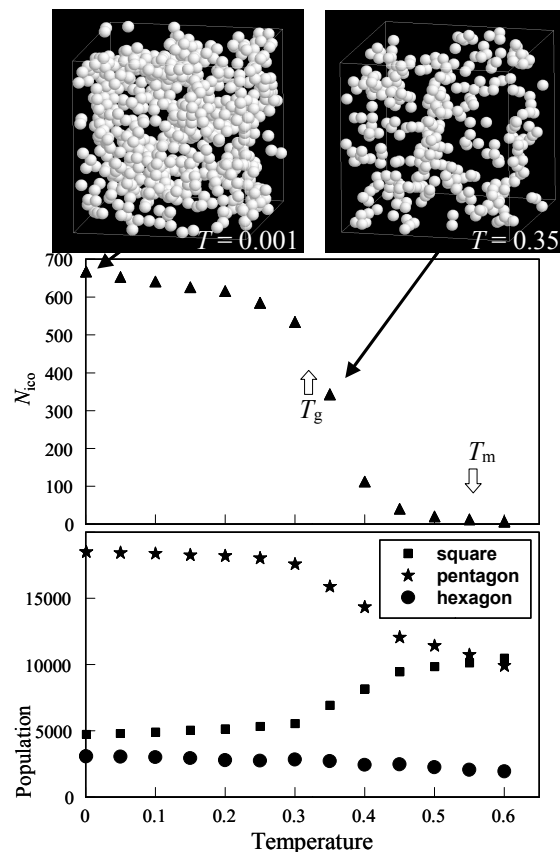

Fig. 2 Temperature dependence of the number N_{ico} of the icosahedral clusters (upper) and that of the population of the Voronoi faces (lower) in the $A_{40}B_{60}$ system during rapid solidification with a cooling rate 2×10^{-4}. The insets at the top are snapshots of the spatial distribution of the icosahedral clusters in different stages of cooling, where the white spheres denote the atoms positioned at the center of the icosahedral clusters.

the Voronoi tessellation analysis [12,13], in which the local symmetry around each atom is indexed by a set (n_3, n_4, n_5, n_6,), where n_i is the number of i-edged faces of the Voronoi cell, we identify the icosahedral clusters by the atoms that have the Voronoi index (0, 0, 12, 0) and their neighbors. The upper part of Fig. 2 shows the temperature dependence of the number N_{ico} of the icosahedral clusters in the $A_{40}B_{60}$ system during the slowly quenched procedure (2×10^{-4}) shown by the closed triangles in Fig. 1. The number of the icosahedral clusters rapidly increases in the strongly supercooled liquid regime just above T_g.

Snapshots of the spatial distributions of the icosahedral clusters are also shown in Fig. 2 by the insets, where only the atoms positioned at the center of the icosahedral clusters are depicted by the white spheres. Both in the strongly supercooled liquid phases ($T = 0.35$) and the glassy phase ($T = 0.001$), some spatial inhomogeneity is found in the distribution of the icosahedral clusters, which indicates a 'clustering' behavior of the icosahedral clusters. The lower part of Fig. 2 shows the time evolution of the population of three dominant types of Voronoi faces, that is, squares, pentagons, and hexagons. Since the population of the pentagons is closely related with the order of the icosahedral symmetry, this result indicates that the icosahedral symmetry already exists even in both equilibrium liquids and weakly supercooled liquids by forming defective or distorted icosahedral clusters not indexed by (0, 0, 12, 0).

Icosahedral Network in Glassy Phases

To clarify the nature of clustering behavior of the icosahedral clusters in glassy phases, we first perform the Voronoi tessellation analysis by regarding the icosahedral clusters as molecules for the $A_{40}B_{60}$ glassy phases. Unfortunately, we cannot find an apparent symmetry in the inter-cluster distribution as found in the reverse Monte Carlo study [8] of glassy alloys of lower solute concentration. Instead, we find a string-like pattern in the inter-cluster packing, as depicted in Fig. 3. Thus we turn to investigate the neighboring nature between clusters.

We can classify the neighboring or linking pattern between two clusters into four categories as shown in Fig. 4, that is, vertex-sharing, edge-sharing, face-sharing, and inter-penetrating or pentagonal bicap-sharing (cap-sharing, in short). Then we calculate the population of each pair for three different glassy phases: an $A_{90}B_{10}$ glass and an $A_{40}B_{60}$ glass prepared by rapid quenching (2×10^{-3}), and an $A_{40}B_{60}$ glass prepared by slow quenching (2×10^{-4}). We have also calculated the population of icosahedral clusters that are linking to other clusters or isolated. The results are shown in Fig. 5, where we can find a clear tendency that the icosahedral network is denser in the glasses of a higher solute concentration and in those obtained by a lower cooling rate. In addition, the dominant linking pattern is the
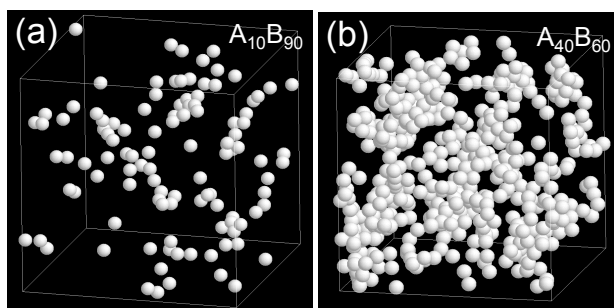

Fig. 3 Snapshots of the spatial distribution of the icosahedral clusters in a $A_{90}B_{10}$ glass (a) and a $A_{40}B_{60}$ glass (b) prepared by rapid quenching (2×10^{-3}). The white spheres denote the atoms positioned at the center of the icosahedral clusters.
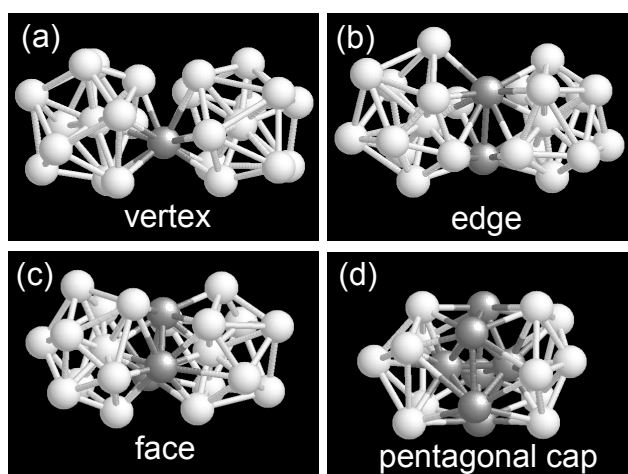

Fig. 4 Snapshots of four types of icosahedral bonding: (a) vertex-sharing, (b) edge-sharing, (c) face-sharing, and (d) pentagonal bicap-sharing. The shared part is denoted by a darker color.
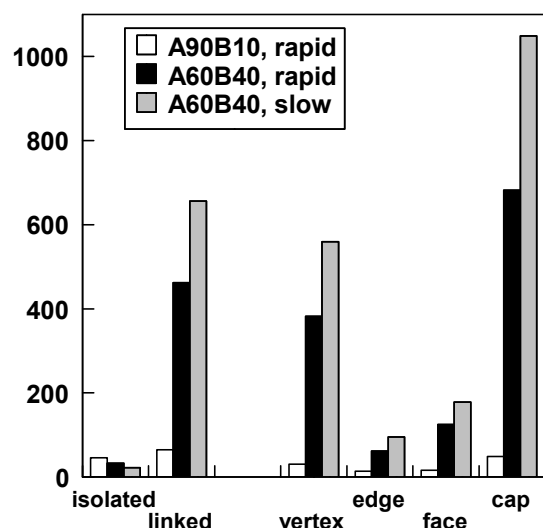
Fig. 5 The population of isolated icosahedra, linked icosahedra, and four different types of bonds in a rapidly quenched $A_{90}B_{10}$ glass, a rapidly quenched $A_{40}B_{60}$ glass, and a slowly quenched $A_{40}B_{60}$ glass.
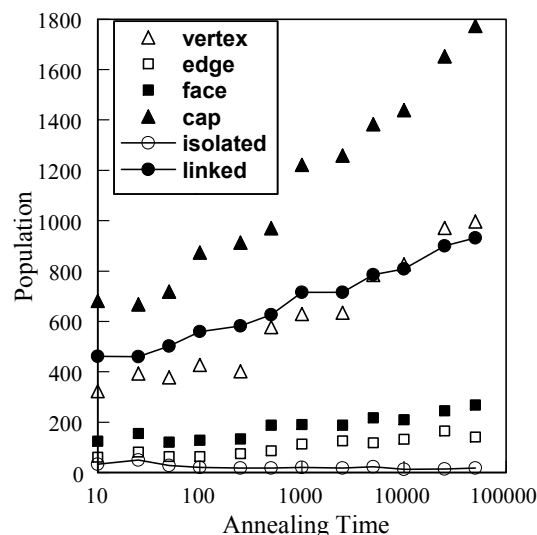

Fig. 6 The change of the population of isolated icosahedra, linked icosahedra, and four different types of bonds in a rapidly quenched $A_{40}B_{60}$ glass, which is isothermally annealed at $T = 0.30$.

cap-sharing in any glasses.

In a similar manner, we calculate the time evolution of the linking morphology in the $A_{40}B_{60}$ glass prepared by rapid quenching, which is isothermally annealed at $T = 0.30$ (just below T_g). The results are shown in Fig. 6. We can also find that the cap-sharing bonds grow and dominate in the glassy phase as the structural relaxation proceeds.

Percolation of Icosahedral Network in Glassy Phases

Previous results indicate that the cap-sharing bonds form a primary structure of the icosahedral network. So we shall focus on the cap-sharing bonds in the glassy phases. Figure 7 shows snapshots of the network of the cap-sharing bonds in the as-quenched $A_{40}B_{60}$ glass (a) and an annealed ($t = 2.5 \times 10^4$) $A_{40}B_{60}$ glass (b). In the annealed glass, the main network extends all over the specimen and apparently percolates, while only fragmental and mutually disconnected networks can be observed in

Fig. 8 Time evolution of the population of two types of structural units in the cap-sharing icosahedral network in the $A_{40}B_{60}$ glass isothermally annealed at $T = 0.30$.
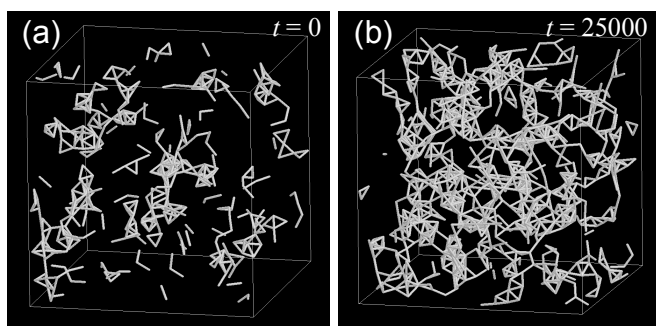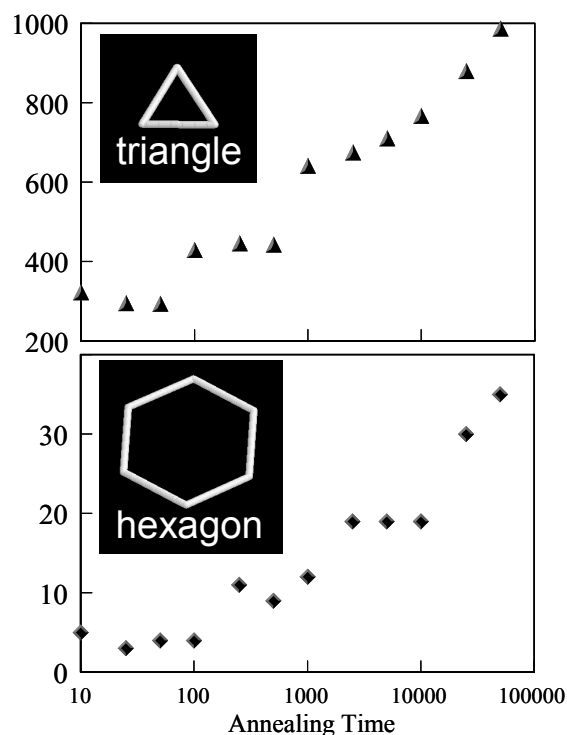

Fig. 7 Snapshots of the spatial distribution of the cap-sharing bonds in the as-quenched $A_{40}B_{60}$ glass (a) and an annealed $A_{40}B_{60}$ glass (b).

the as-quenched glass. The network formed by the cap-sharing bonds is exactly corresponds to the 'no disclination line' in a geometrical description of the dense random packing structure by Nelson [14], so the extension of the network indicates a decrease of frustration in the system.

If we pay a special attention on the specific morphology of the network depicted in Fig. 7(b), we can find two types of characteristic shape, that is, triangles and hexagons. Then we calculate the time evolution of the population of these units during annealing. The results are shown in Fig. 8. The drastic increase of these two units with the annealing time indicates that these units should play an essential role to stabilize the icosahedral network in the glassy phases.

Summary

By performing the MD simulations for a model alloy system, we have clarified the following points: (1) the icosahedral short-range order grows both in the supercooled liquids and glassy phases, (2) the network formed by the icosahedral clusters mutually bonding via the pentagonal bicap-sharing is an origin of a medium-range order in the glassy phases, and (3) the connectivity of the icosahedral network increases in the relaxation processes of the glassy phases and it brings a percolation of the main network. We think that the cap-sharing network of icosahedral clusters is a key structure to understand the MRO and the stability of the metallic glasses.

Acknowledgements

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