Free-Energy Analysis of the Zr–Ni–Al Bulk Metallic Glass from the Local Atomic Arrangements of the Relevant Crystals

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Free-energy of Zr–Ni–Al bulk metallic glass (BMG) was estimated by making full use of coordination clusters in the relevant crystals. The clusters in the BMG were determined by using the BMG’s experimentally determined radial distribution functions, and the electronic structure of the identified clusters was calculated by the DVX cluster calculation. The local atomic arrangements in the Zr–Ni–Al BMG are found to be characterized by the prism clusters with Zr or Ni atom in their center and the Kasper polyhedrons about Al atoms. It was conclude, as a consequence of the present analysis, that the Zr–Ni–Al BMG are stabilized by the low internal-energy of the constituent local atomic clusters assisted by the large entropy caused by the freedom in the bond-direction between the prism clusters and the Kasper polyhedrons.

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1. Introduction

Recently bulk metallic glasses (BMG’s) have attracted a great deal of interests because of their ability in practical usage, such as mechanical parts of high strength, surface coating materials with high degree of hardness, and soft-magnetic materials.1–37 BMG’s are characterized by a wide temperature range of \( T_G < T < T_X \) and narrow temperature range of \( T_X < T < T_M \), where \( T_G \), \( T_X \), and \( T_M \) indicate the grass-transition temperature, crystallization temperature and melting temperature, respectively.4–11) These conditions enable us to easily obtain the super-cooled liquid state even with relatively slow cooling rate, and that the amorphous phase in the bulk shape is easily obtained. One may naturally expect that the BMG’s would have fairly low free-energy and large activation energy for the crystallization, though the mechanism leading to these conditions has not been clarified yet. In sharp contrast to difficulty in investigating the activation energy, free-energy of the BMG’s could be analyzed on the basis of the idea described below.

Free-energy is determined by internal-energy and entropy. Internal-energy in metallic solids is generally dominated by the metallic bonds, which prefers densely packed structure.15) However, if the system contains transition metal elements, covalent bonds due to the partially filled \( d \)-orbitals of the transition metal elements often contribute to reduce internal-energy of the metallic solids by forming bonding-states below the Fermi level \( (E_F) \). In such a case, local atomic arrangements with characteristic coordination of the atoms are generally observed.

Since the covalent bond provides short range ordering, it can reduce the internal-energy of amorphous phase as well as that in the relevant crystals. Entropy, on the other hand, plays a very important role only in stabilizing amorphous phases in sharp contrast to its less important role in the crystalline materials. Since BMG’s are obtained in the metallic system with transition metal elements, we believe that the BMG’s would have local atomic clusters similar to those in the relevant crystals that possess low internal-energy because of the covalent bonds. Those characteristic local atomic clusters are supposed to be randomly arranged so as the entropy of the BMG’s to become maximal. Consequently, the free-energy the BMG’s are reduced to be comparable with that of the crystals in the same alloy system.

In order to confirm the validity of this scenario, we investigated, in this study, the local atomic arrangements of the relevant crystals, and compared them with the experimentally determined local atomic arrangements of the Zr–Ni–Al BMG. The internal-energy of the clusters was estimated using the first principle cluster calculation and the high resolution photoemission spectroscopy. The composition dependence of entropy was also discussed by analyzing entropy of the cluster arrangements. In this way, we gained deep insight into the origin of the low free-energy, that is one of the most important factors for the stabilization mechanism of BMG’s.

2. Experimental Procedure

Relevant crystals in the Zr–Ni–Al ternary alloy system were prepared by induction melting under the pressurized Ar atmosphere. All ingots were annealed at 800°C for 24 h to remove the strain and imperfections in the crystal structure. The phases in the ingots were investigated by the conventional powder X-ray diffraction with CuKα radiation source. The ingots consisting only of a single relevant crystal were used for the photoemission measurements.

Radial distribution functions, RDF’s, were determined
by using neutron and X-ray diffraction measurements. Details of the analyses were reported elsewhere. 13) The results of the diffraction measurements on the Zr–Ni–Al BMG will be presented elsewhere in near future. 14)

High-resolution photoemission spectroscopy measurements were performed at 10 K using the MBS scientific A-1 analyzer placed at the ultra violet photon beam line BL5U in UVSOR, Okazaki, Japan.

The clean sample surfaces were prepared by fracturing bulk ingots under a ultra high vacuum better than $2 \times 10^{-8}$ Pa. We used incident photon energy of 20 eV for the photoemission measurement. The total energy resolution was $\Delta E \sim 20 \text{meV}$ that was estimated from the Fermi edge of the reference gold electrically contacted with the samples.

3. Results and Discussions

3.1 Structure

Figure 1(a) shows the contour plot of $\Delta T_X = T_X - T_G$ for the Zr–Ni–Al BMG reported by Hasegawa et al. 15) together with the compositions of the thermodynamically stable crystalline phases. The maximum $\Delta T_X$ was located at the composition of Zr$_{55}$Ni$_{28.6}$Al$_{10}$ where no crystalline structure is stabilized as a single phase. This characteristic indicates the importance of entropy in stabilizing BMG’s.

We consider, as the first approximation, that the coordination polyhedrons play the role of the “structure-units” constructing the BMG’s. The coordination polyhedrons persisting in the relevant crystals were extracted from the structure parameters in the Pearson’s handbook. 16) It should be stressed here that the most difficult part in the present analysis was estimation of the composition of polyhedrons, because those coordination polyhedrons always share their outer atoms with others, and sometimes penetrate with each other. We assume here that each atom on the cluster surface provide a fraction $(1/N_{\text{coor}})$ of itself, where $N_{\text{coor}}$ indicates the coordination number of the atom on the cluster surface. Let us consider that a X atom in the center of the cluster is surrounded by X, Y and Z atoms of $(N_x, N_y, \text{ and } N_z)$ and $(N_{x\text{coor}}, N_{y\text{coor}}, \text{ and } N_{z\text{coor}})$ in number and coordination number, respectively. The composition of the cluster is calculated by the chemical formula of $X(1 + N_x/N_{x\text{coor}})Y(N_y/N_{y\text{coor}})Z(N_z/N_{z\text{coor}})$. For a typical example, we explain the case of ZrNi$_2$Al possessing three atomic sites, Al-site, Ni-site, and Zr-site. The Al-site is surrounded by eight Ni atoms and six Zr atoms. By considering that all the surrounding Ni and Zr atoms have a coordination number of $N_{\text{coor}} = 14$, we calculated the composition of the cluster as Zr$_{50}$Ni$_{28.6}$Zr$_{21.4}$ from Al + $(8/14)$Ni + $(6/14)$Zr. The compositions of the coordination clusters centered at the Ni- and Zr-sites in the ZrNi$_2$Al are also calculated to be Al$_{14.3}$Ni$_{71.4}$Zr$_{14.3}$ and Al$_{21.4}$Ni$_{28.6}$Zr$_{50}$, respectively. The validity of the calculated cluster-compositions can be confirmed by knowing that the composition of the original crystal is reproduced by adding the cluster-compositions with the ratio of clusters in the original crystal; the sum of the cluster compositions, Al$_{50}$Ni$_{28.6}$Zr$_{21.4}$ + 2 × Al$_{14.3}$Ni$_{71.4}$Zr$_{14.3}$ + Al$_{21.4}$Ni$_{28.6}$Zr$_{50}$, results in ZrNi$_2$Al. Those operations are schematically illustrated in Fig. 2.

The unit structures containing an atom and fractions of the neighboring ones are considered as the “quasi-atoms”. Since the number of atoms in each quasi-atom is roughly estimated to be two, the entropy associated with their random arrangements would be reduced by factor of $\sim 1/2$ from that of the random-arrangements of the atoms because of the reduction in number of the structure units. The BMG’s must have these quasi-atoms as their structure units when the energy reduction associated with the quasi-atoms formation exceeds the increase of the free energy due to the reduction in the entropy. The contribution of the entropy and the energy reduction due to the cluster formation will be discussed below in detail. Although the idea of the quasi-atom mentioned above is very important, we decided to keep using the words “coordination clusters” rather than using

Fig. 1 (a) Zr–Ni–Al composition diagram with contour line of $\Delta T_X = 30$, 50, and 70 K. Solid circles indicate compositions of crystalline phases. Solid stars indicate the composition where the largest $\Delta T_X$ is observed [REF15]. (b) Zr–Ni–Al composition diagram with compositions of the coordination clusters in the crystalline phases. Circles, triangles, and squares indicate the composition of Zr-centered, Ni-centered, and Al-centered coordination clusters, respectively. Compositions of the coordination clusters identified to exist in the BMG are shown with solid markers.
“quasi-atoms” in the following sections for the sake of simplicity.

Figure 1(b) shows the Zr–Ni–Al composition diagram of the coordination clusters. Coordination clusters are classified into three groups by their center atom, and are shown with different markers. Obviously composition of the Al-centered clusters stays in Al-rich region, and composition of the Zr-centered and Ni-centered clusters in Zr-rich and Ni-rich regions, respectively.

Here we employed the radial distribution function, $RDF(r)$, to pick up the clusters that exist in the Zr–Ni–Al BMG. $RDF(r)$’s about Zr, Ni, and Al of the Zr–Ni–Al BMG were determined by the neutron and X-ray diffraction measurements with the reverse Monte Carlo simulation (RMS). By calculating $RDF(r)$’s from selected sets of the coordination clusters, we confirmed that the experimentally determined $RDF(r)$’s can be qualitatively reproduced by the $RDF(r)$’s calculated from the coordination clusters. The resulting $RDF(r)$’s were shown in Fig. 3 with the experimentally determined ones. This experimental fact indicates that the local atomic arrangements of the relevant crystals exist in BMG’s.

We found that the local atomic arrangements around Zr atoms in the Zr–Ni–Al BMG are reproduced by two coordination clusters both of which exist in the InMg$_2$-type hexagonal Zr$_6$NiAl$_2$. These two coordination clusters about Zr atoms have a shape of pentagonal and quadrilateral prisms. It is also very important to note that the Zr$_6$NiAl$_2$...
stabilizes in the vicinity of the composition where the largest ΔT_X is observed.\textsuperscript{15)}

\textit{RDF}(r) about Ni was not reproduced by the coordination clusters in a unique relevant crystal but by three coordination clusters from three different relevant crystals; the orthorhombic \textit{B}Cr-type ZrNi(oC8), the Fe\textsubscript{2}P-type hexagonal ZrNiAl(hp9), and the InMg\textsubscript{2}-type hexagonal Zr\textsubscript{6}NiAl\textsubscript{2}(hp9). The structure of the Fe\textsubscript{2}P-type ZrNiAl is almost the same with that of the InMg\textsubscript{2}-type hexagonal Zr\textsubscript{6}NiAl\textsubscript{2}(hp9); one of the atomic sites denoted as (1/4, 0, 0) in the InMg\textsubscript{2}-type structure slightly moves along the a axis in the Fe\textsubscript{2}P-type structure without altering the number of atoms in the unit cell. All of the identified clusters about the Ni atoms were classified into a group of triangular prisms.

The clusters about an Al atom in the Zr–Ni–Al BMG are identified as a prism, a CN12 Kasper polyhedron,\textsuperscript{17)} and a CN11 pseudo Kasper polyhedron. The structure of the CN11 pseudo Kasper polyhedron is understood as that of the CN12 Kasper polyhedron lacking for one of the twelve atoms at the surface. Those clusters can be found in ZrNiAl(hp9), Zr\textsubscript{6}NiAl\textsubscript{2}(cF24), and Zr5Al\textsubscript{3}(hp16).

The identified coordination clusters are schematically illustrated in Fig. 4, and their compositions are shown with the solid markers in Fig. 1(b).

### 3.2 Electronic structure and internal-energy

The energy reduction associated with the formation of the characteristic cluster levels was calculated using the DVX\textit{α} cluster calculation method.\textsuperscript{18)} Atoms on the surface of the clusters would have a fairly different electronic structure from those in a bulk sample. Therefore only the electronic structure of the center atom was extracted from the calculated cluster orbitals.

Generally \textit{d}-orbitals in solids produce bands well approximated by the tight-binding functions. In such a case, nature of the atomic orbitals is kept remained and the eigen-values of the Bloch states in each band are limited within a very narrow energy range. The energy of these bands, therefore, can be quantitatively predicted by the DVX\textit{α} cluster calculation method. Electronic structure of the \textit{s}, \textit{p}-bands, on the other hand, is hardly predicted by the cluster calculation because \textit{s}, \textit{p}-bands are widely distributed in the real space with plane-wave like wave functions and their eigen-values significantly vary with momentum. Thus we intentionally avoided calculating the cluster orbitals of Al atom in the center of the clusters.

We calculated the cluster orbitals in the pentagonal and quadrilateral prism clusters with a Zr atom in its center and the triangular prism clusters with a Ni atom in the center. The CN12 Kasper polyhedron cluster with a Ni atom in the center, that is absent from the structure of the Zr–Ni–Al BMG, was also employed to compare its cluster orbitals with those in the other clusters existing in the BMG. We obtained partial electronic density of states of the \textit{d}-orbitals of the center atom by multiplying each calculated cluster level by a Lorentzian function of 1.0 eV in energy width. The resulting spectra are shown in Fig. 6.

The energy reduction associated with the \textit{4d}-orbitals of the Zr-atoms in a prism cluster is easily predicted by the following consideration. The coulomb potential induced by the neighboring atoms at the vertices of the prism structure leads to a splitting of the Zr \textit{4d} states into roughly two groups of different energy, \{\textit{d}_{z^2}, \textit{d}_{x^2−y^2}\} and \{\textit{d}_{x^2}, \textit{d}_{y^2}, \textit{d}_{z^2}, \textit{d}_{xy}\} of high and low energies, respectively. Each group produces bonding and anti-bonding states with orbitals of the surrounding atoms, and four peaks are supposed to be produced in the Zr \textit{4d} partial density of states. Since each Zr atom in solid provides one or two \textit{d}-electrons into the valence band, all \textit{d} electrons fall into the bonding states, and consequently internal-energy associated with the prism cluster is reduced drastically. Indeed, calculated Zr \textit{4d} partial density of states (\textit{N}_Zr\textit{4d}(\textit{E})) of the two different prism clusters possesses four peaks as we predicted above. The energy gain caused by the cluster orbital formation was estimated by subtracting energy of the Zr \textit{4d} states in an isolated Zr atom from that of the identified clusters. The total kinetic energy of the Zr \textit{4d} electrons is reduced by \raise0.5ex\hbox{\boldmath$\sim$}1.73 eV. This energy reduction must lead to stabilization of this local atomic arrangements; prism clusters with a Zr atom in their center.

The neighboring atoms around Ni atoms in the Zr–Ni–Al...
BMG were found to construct triangular prisms. The Ni 3d-orbitals in the center of the triangular prism would have nearly the same configuration of the cluster levels with that of the previously described 4d orbitals in the center of the pentagonal prism. Thus, four different cluster levels are roughly predicted in the Ni 3d partial density of states. However, only three peaks are observable in the calculated Ni 3d partial density of states (N_{Ni3d}(E)) in the center of the triangular prism. Reduction in number of peaks is most likely caused by that two of four peaks overlapped together because of the small values of the transfer integral of 3d orbitals. The Fermi level (E_F) moves up into one of the anti-bonding states that stays above the 3d level of the isolated Ni atom because the number of the Ni 3d electrons exceeds half of the total d-states. One may naturally consider that this situation causes an increase in the total kinetic energy of Ni 3d states. Surprisingly, however, we found that the total energy of the Ni 3d states is significantly reduced by $\sim -2.3$ eV per Ni atom. This large reduction in the total energy of the Ni 3d states is brought about by the large peak located at $-3\ldots-2$ eV that is much lower than the energy of the Ni 3d level in the isolated Ni atom. The resulting energy reduction, $-2.3$ eV, indicates very strong tendency of stabilization due to the local atomic arrangements; triangular prisms with a Ni atom in their center.

At the center of the CN12 Kasper polyhedron that is absent from the BMG, the d-orbitals of the Ni atoms show no characteristic energy-splitting but simply provide two different energy levels corresponding to the bonding- and anti-bonding states constructed with the atomic orbitals of the surrounding atoms. Thus two peaks are produced in the partial density of states. Indeed, the calculated $N_{Ni3d}(E)$ of the center of the CN12 Kasper-polyhedron has two major peaks, one of which is almost identical to that of the isolated Ni atom and the other is located at slightly lower energy with smaller intensity. Energy reduction was estimated to be...
-1.6 eV, and this value is certainly smaller than that of $d$-orbitals in the prism cluster. This results strongly let us believe that less significant energy reduction prevents the CN12 Kasper polyhedron with a Ni atom in its center from persisting in the Zr–Ni–Al BMG.

In order to further confirm the reliability of the present analysis on the electronic structure, we employed here the high-resolution photoemission spectroscopy measurements for the selected relevant crystals. Figures 6(a), (b), and (c) show high-resolution photoemission spectra of Zr$_6$NiAl$_2$, ZrNi, and ZrNiAl, respectively. All compounds possess prism structure about Zr and Ni, which were identified to as structure units in the Zr–Ni–Al BMG. The DVX$\alpha$ cluster calculation for these prism clusters with Zr/Ni in its center predicted large/small peak just below $E_F$ and small/large one at about -2 eV as shown in Fig. 6. Indeed, two peak/hump structures of 1–2 eV in width were observed in all photoemission spectra at about 0.5 and 2 eV below $E_F$. By considering difference in Zr and Ni concentrations in these compounds, we safely assigned that the structures at -0.5 and -2 eV are dominated by Zr 4$d$ and Ni 3$d$ components, respectively. Thus it is argued that the reliability of the cluster calculation was successfully confirmed by the present photoemission spectroscopy.

Unfortunately, however, it was impossible to completely extract Zr 4$d$ and Ni 3$d$ partial density of states from the photoemission spectra accumulated only with the incident photon energy of $h\nu = 20$ eV. Further experiments, such as resonant photoemission spectroscopy with varying incident photon energy, should be performed to gain deeper insight into nature of each partial density of states. Those experiments are now in progress and will be reported in near future.

3.3 Entropy

Present analysis on the local atomic clusters revealed that some of the clusters extracted from the relevant crystals do exist in the BMG’s because of their small internal energy. The prism clusters with a Zr or Ni atom in their center were revealed to possess a small internal energy, and those clusters persist in the Zr–Ni–Al BMG. The clusters with an Al atom in their center in the Zr–Ni–Al BMG are identified mainly as the Kasper-polyhedrons, in which atoms are stacked with each other in the manner of the tetrahedral close packing.

By carefully observing these identified clusters, we found an important fact that the Kasper polyhedrons can connect...
the prism clusters because the prism clusters have tetrahedral atomic arrangements that correspond to the local atomic arrangements in the Kasper polyhedrons. (See Fig. 7) It is also very important to know that the Kasper polyhedrons provides a large freedom in the bond-direction; twenty almost equivalent bond-direction in the CN12 Kasper polyhedrons. Thus the freedom in the bond direction between the Kasper polyhedrons and the prisims is considered to be responsible for the random network of the clusters and consequently for the large entropy. In this model, the prism clusters produce a three-dimensional-network with sharing the atoms in their vertices. The edge sharing of the prism clusters and penetration of the clusters would also takes places with a help of the other Al-centered prism, and those connections of the clusters further enhance the randomness of the cluster connections.

This model for the BMGs’ structure can be expressed, in other words, that the clusters with covalent nature are connected with the glue atoms of metallic nature so as to be randomly arranged in the BMG’s. The presence of the endothermic reaction with increasing temperature, that is known as the glass-transition at $T_G$, is accounted for with this model of two different chemical characters. The internal energy of the clusters with covalent nature would be highly stable and rigid at high temperatures even above $T_G$. The glue clusters, on the other hand, would start to expand and plays as a source of endothermic reaction when the thermal energy becomes comparable with the metallic-cohesive energy of the clusters at $T_G$.

Here we estimate the composition dependence of the entropy $S$ using the following formula.

$$S = N \cdot k_B \sum x_i \ln(1/x_i)$$

(1)

$N$, $k_B$ and $x_i$ represent the number of the structure units, the Boltzmann’s constant, and concentration of the components, respectively. Coordination clusters identified in this paper were considered to be the structure units of the BMG. The concentration of the clusters $x_i$ was calculated from $N_i/N_{\text{cluster}}$, where $N_{\text{cluster}}$ and $N_i$ indicate the total number of the clusters (quasi-atoms) in the sample and the number of a specified cluster, respectively. We have to remember that entropy associated with positions and orientations of the clusters (quasi-atoms) was not taken into account in eq. (1). Although it is not trivial, we ignored the contribution of cluster position/orientation to entropy because freedom in the cluster position/orientation is supposed to have less significant composition dependence in the BMGs.

The calculated $S$ becomes maximal near the center of the ternary composition diagram because the maximum of $S$ always appears at the center of balance for the polygon of the cluster compositions constructed on the ternary phase diagram. The Zr rich concentration of the BMG’s possessing large $\Delta T_G$ is located at large Zr concentration range. This experimental fact indicates smaller internal-energy of the Zr-centered clusters than that in the other clusters. One may wonder that this argument is inconsistent with the calculated energy reduction of clusters; 1.7 eV for the Zr-centered and 2.3 eV for Ni-centered prism clusters. This inconsistency would be caused by the energy reduction associated with metallic bond that was not taken into account in the present cluster calculation. In order to investigate the energy gain in more detail, we have just started to employ the first principle band calculation, with which cohesive energy associated with metallic bond can be quantitatively investigated. Results of the first principle band calculation will be reported in near future.

We have to also mention that the newly introduced idea of the constituent clusters (quasi-atoms) reduces the number of constituent units by a factor of $\sim 1/2$, as it was discussed in Structure. The entropy of the system is consequently reduced by the factor of $\sim 1/2$, provided that variations both in positions and orientations of the pseudo-atoms are similarly treated as those of the constituent atoms. Although this reduction in the entropy due to the formation of the characteristic clusters leads to an increase in the free-energy of the BMG, internal-energy reduction associated with the cluster formation effectively reduces free-energy of the BMG. This must be the reason for the presence of the characteristic clusters. Quantitative evaluation of the total entropy should be performed to prove the argument described.
above. Unfortunately, however, the absolute value of the total entropy cannot be estimated in this particular stage because of lack of information about the variations in positions and orientations of atoms. Further analyses on the entropy, such as that used in the CALPHAD,\textsuperscript{18,19} should be employed to fully understand the free-energy estimation of the BMG’s.

4. Conclusion

Local atomic arrangements of the Zr–Ni–Al bulk metallic glass were investigated by the cluster analysis in the relevant crystals. Clusters in the BMG were characterized by the prism structure about the transition metal elements and the Kasper polyhedrons about Al atoms. The reduction in the internal energy associated with cluster formation was estimated by the DVX\textsubscript{α} cluster calculation, and the prism structure with a transition metal element in its center was found to have very low internal-energy. The reliability of the cluster calculation was confirmed by the high-resolution photoemission spectroscopy for the relevant crystals. We propose, as a consequence of present analyses, that the structure of the Zr–Ni–Al BMG is well accounted for by the prism clusters about transition metal elements with being connected by the Kasper polyhedrons of metallic nature. The connection between prisms and Kasper polyhedrons has freedom in bond direction, and therefore the entropy of the cluster configuration is significantly increased. Combination of the low internal-energy of the clusters and large entropy of the cluster configuration leads to the stabilization of the BMG by reducing its free-energy.

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