Ab-Initio Data for Interatomic Interactions in Zr-Rich ZrX (X = Sc-Cu) Alloys and Stability of Icosahedron-Like $\text{Zr}_{13-n}\text{Cu}_n$ ($n = 3, 4$) Clusters in $\text{Zr}_{70}\text{Cu}_{30}$ Metallic Glass

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We give ab-initio data for the study of the stability of the atomic structures of Zr-rich ZrX (X = Sc-Cu) alloys, such as the cohesive energies and equilibrium Wigner-Seitz radii of elemental metals X (X = Sc-Cu, Zr-Ag) and X-X (X = Sc-Cu) interaction energies in Zr. The calculations are based on the density functional theory in the generalized gradient approximation and employ the full-potential Korringa-Kohn-Rostoker Green's function method. Using the calculated results, we elucidate the fundamental features of interatomic interactions of Zr-rich ZrX alloys. Especially, we found that the pair interaction of Cu impurities in Zr becomes strongly attractive around the interatomic distance of 0.45~0.46 nm. It is shown that this interaction may be important for the stability of icosahedron-like local atomic structures of $\text{Zr}_{10}\text{Cu}_3$ and Zr_9Cu_4 clusters in the $\text{Zr}_{70}\text{Cu}_{30}$ bulk metallic glass, being proposed experimentally. We also found that the atomic structure of an isolated Zr_{10}X_3 cluster transforms from the hcp structure (initial state) to an icosahedron-like structure (final state) for X = Cu, but not for X = Ni. [doi:10.2320/matertrans.MJ200743]

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1. Introduction

The stability of $\text{Zr}_{70}\text{Cu}_{30}$ bulk metallic glass (BMG), may be characterized by the high stability of local atomic structures which never exist in the crystalline phases. Saida *et al.* recently proposed experimentally that the high stability of the $\text{Zr}_{70}\text{Cu}_{30}$ BMG may be due to the existence of the icosahedron-like (icos-like) local atomic structure.^{1,2)} Although there are now many experimental data for the local atomic structures for BMGs, it is still difficult to determine the local atomic structures in non-periodic alloys such as BMGs, directly from the experimental data. Thus, the theoretical study is strongly requested for the interatomic interactions in BMGs, which are essential for the elucidation of the physical mechanism of the stability of BMGs and may be important for the materials design of new BMGs.

At present we can perform ab-initio calculations for ordered alloys with a number of atoms (less than 100 atoms) per unit cell in order to understand the physical mechanism of the stability of their experimentally-known atomic structures. It is also possible to calculate the interatomic interaction energies of agglomerates of impurities (less than 100 atoms) in elemental metals as well as the total energies of ordered alloys.^{3,4)} Although highly accurate for predicting alloy properties, the ab-initio calculations are limited to relatively small systems. The direct application of the ab-initio calculations to the determination of the atomic structures of large-scale non-periodic systems such as BMGs is clearly impossible.

Thus, under these circumstances, we have proposed the cluster expansion approach (CEA) for cohesive energies of alloys, which allows one to study the stability of the different atomic structures of alloys.^{5,6)} We have shown that the chemical trends of relative structural stability of the Al_3X (X = Sc, Ti, V) ordered alloys, together with the Mackay

icosahedron in the $\text{Al}_{80}\text{Mn}_{20}$ quasicrystal, are understood by considering the distance dependence of the strong, oscillating, and long-ranged X-X interaction energies in Al: for example, the Mackay icosahedron in the $\text{Al}_{80}\text{Mn}_{20}$ quasicrystal may be stabilized by the strong attraction which occurs at the Mn-Mn distance in the Mackay icosahedron.⁵⁾ The interaction energies were calculated accurately by the ab-initio method based on the full-potential Korringa-Kohn-Rostoker (FPKKR) Green's function method and the density functional theory in the generalized gradient approximation (GGA).⁵⁾

In the present work, we apply the same approach to the study of the characteristic features of interatomic interactions of the Zr-rich ZrX (X = Sc-Cu) alloys and try to elucidate the physical mechanism of the strong stability of the $\text{Zr}_{70}\text{Cu}_{30}$ BMG. We have found that the Cu-Cu interaction in Zr is strongly attractive around the interatomic distance of 0.45~0.46 nm. This interatomic distance may be close to the second-neighboring Cu-Cu distance in an icos-like $\text{Zr}_{10}\text{Cu}_3$ cluster (see Fig. 1 in Ref. 2). We have also found that the atomic structures of an isolated Zr_{10}X_3 (X = Cu, Ni) cluster transforms from the hcp structure to an icos-like local structure for X = Cu, but not for X = Ni. We also discuss the stability of an icos-like Zr_9Cu_4 cluster, which is stoichiometrically closer to the $\text{Zr}_{70}\text{Cu}_{30}$ BMG.

2. Calculation Method

We briefly discuss the calculational procedure for the interatomic interaction energies of Zr-rich ZrX alloys, because the details are discussed in Refs. 3) and 6). In the present CEA we consider the minority element (X) as impurities and the majority element as the bulk atoms, and decompose the cohesive energies of Zr-rich ZrX alloy into three components: (1) cohesive energies of Zr and X metals;

Fig. 1 (a) Atomic structures, Wigner-Seitz radii, and (b) cohesive energies of Sc-Cu and Zr-Ag.

(2) one-body interaction energy (IE) in Zr, corresponding to the solution energy of a single X impurity in Zr;⁷⁾ (3) two- and many-body IEs in Zr. All the terms may be determined uniquely and successively, from low-order to high-order, by using the set of total energies of isolated Zr and X atoms, pure Zr and X metals, and agglomerates of X impurities in Zr. The calculations for total energies of all the systems considered here are based on the density functional theory in the GGA. In order to solve the Kohn-Sham equation, we use the all-electron FPKKR Green's function method. The advantage of KKR-Green's function method is that, by introducing the host structure-Green's functions, the embedding of point defects in an otherwise ideal crystals is described correctly, differently from the usual supercell and cluster calculations. Another advantage is that we can now use the screened FPKKR calculations⁸⁻¹⁰⁾ for ordered alloy, which simplify the numerical calculations for the total energies and the Green's functions in the host structure. Thus, we can treat the impurity systems in the ordered alloys with 10~20 of atoms per unit cell. It is also possible to study the lattice distortion effect, which is important for the systems with impurities of large atomic-misfit, compared with the host atom.¹¹⁻¹³⁾

3. Calculated Results

In order to study the characteristic features of interatomic interactions of elemental metals X (X = Sc-Cu) and their alloys, in 3.1 we show the calculated results for atomic structures, equilibrium Wigner-Seitz radii, and cohesive energies of elemental metals Sc-Cu: the calculated results for Zr-Ag are also shown for comparison. The atomic structures of ground state are determined by the comparison of the total energies of three structures (fcc, hcp, bcc), one of which is the observed ground-state atomic structure of the elements considered here, except Mn; for the sake of

simplicity we neglect the observed ground-state structure for Mn. In 3.2, we show the X-X (X = Sc-Cu) interaction energies in Zr metals and discuss the stability of icos-like $\text{Zr}_{10}\text{Cu}_3$ and Zr_9Cu_4 clusters in $\text{Zr}_{70}\text{Cu}_{30}$. In 3.3, we show the stable atomic structures of isolated Zr_{10}X_3 (X = Cu, Ni) clusters, obtained by the STO-basis set ab-initio calculations,¹⁴⁾ which may give the information of interatomic interactions in Zr_{10}X_3 (X = Cu, Ni) clusters.

3.1 Cohesive energies and Wigner-Seitz radii for X = Sc-Cu, Zr-Ag

Figure 1 shows the calculated results for the atomic structures, cohesive energies, and Wigner-Seitz radii for elemental metals Sc-Cu, and Zr-Ag as well as the experimental results: for Mn, the hcp structure is the most stable among fcc, hcp, and bcc structures. It is noted that the experimental results are reproduced very well by the present ab-initio calculations. The micro-mechanism of large values and parabolic behavior of cohesive energies 3d and 4d series as well as the strong dip in the middle of 3d series, being seen in Fig. 1, were already explained.¹⁵⁾ It is also obvious that the smallness of Wigner-Seitz radii and cohesive energies of 3d elements, compared with 4d elements, is due to the stronger localization of 3d orbitals compared with 4d orbitals, resulting in the smaller hybridization with the neighboring orbitals. However, the cohesive energy of Ni is not so small as that of Cu. This difference is explained by considering the localization of 3d orbitals: the 3d orbital of Ni is not so strongly localized as that of Cu. It is also expected that the pairing of Zr with Ni makes a stronger bonding because of Friedel's band-filling: the d-bonding states of Zr-Ni are just full-occupied by the pairing of Zr and Ni (the d-electrons are ~8 for Ni and ~2 for Zr). Thus, the fundamental features of interatomic interactions may differ profoundly even though Cu and Ni are the nearest neighbors in the periodic table.

Figure 2 shows the distance-dependence of X-X interaction energies in Al-fcc, from 1st to 8th neighbors as shown in Fig. 3(a). For early 3d and 4d elements the interatomic interactions are long-ranged because of the delocalization of d orbitals. For example, the Zr-Zr interaction in Fig. 2(b) is very long-ranged and oscillating: we can see a strong repulsion around 0.5 nm. Although the detailed behavior depends on the host, the fundamental feature of interatomic interactions, such as long-ranged and oscillating behavior, may remain. The stability of a hcp structure of Zr metal, compared with a fcc structure, may be due to this long-ranged interatomic interaction: it is noted that the coordination numbers in hcp and fcc structures (Figs. 3(a) and (b)) are the same up to the 2nd-neighbor. We also expect that the high stability of Zr-rich ZrCu BMG¹⁾ is in part due to this Zr-Zr long-ranged and oscillating interaction, because the substitution of Cu may stabilize Zr-rich alloys by eliminating the repulsive part in the Zr-Zr long-ranged interaction.

3.2 X-X (X = Sc-Zn) interaction energies in Zr

Figure 4 shows the calculated results for X-X (X = Sc-Cu) interaction energies in Zr-fcc. In the present work, we neglect the spin-polarization effect, although the ground states of X (= Cr, Mn, Fe, Co) impurities are magnetic in Zr. The spin-polarization effect, being not important for the present

Fig. 2 Distance dependence (1st to 8th in Fig. 3(a)) of X-X ($X = \text{Sc-Cu}$, Y-Ag) interaction energies in Al-fcc.

discussion, is published elsewhere.¹⁶⁾ The main characteristic feature is that the X-X interactions are strongly attractive (~ -0.1 eV) around $0.45\sim 0.46$ nm (2nd-neighbor distance) and strong repulsive around $0.53\sim 0.64$ nm (beyond 2nd-neighbor distance), for $X = \text{Co, Ni, and Cu}$. Thus, it is easily expected from the view point of the pair interaction energy that the atomic structures of Zr-rich ZrX alloys are rearranged to increase the number of X-X pairs with the interatomic distance $0.45\sim 0.46$ nm and to decrease the

Fig. 3 Atomic structures of (a) a fcc metal, (b) a hcp metal, (c) an isolated hcp Zr_{10}X_3 cluster, and (d) an icosahedron Zr_{10}X_3 cluster.

number of X-X pairs with the interatomic distance $0.53\sim 0.64$ nm.

Figure 5 shows the comparison of X-X ($X = \text{Cu, Ni}$) interaction energies in Zr-fcc and Zr-hcp: it is noted that there are two kinds of 1st (1 and 1') and 4th (4 and 4') neighbors in the hcp structure (2 atoms per unit cell), as shown in Fig. 3(b). In Zr-hcp, the pair interaction energy abruptly increases around 0.53 nm where no corresponding distance exists in the fcc structure. The other feature of X-X interactions in Zr-hcp is similar to that in Zr-fcc.

Now we discuss how the Cu-Cu strong attraction around $0.45\sim 0.46$ nm is important for the stability of an icos-like local structure of $\text{Zr}_{10}\text{Cu}_3$, being proposed experimentally^{1,2)} and discuss why the icos-like structure is not observed in Zr-rich ZrNi alloys.

According to the experiments of the $\text{Zr}_{70}\text{Cu}_{30}$ BMG,¹⁾ the Zr-Cu bond distances are distributed broadly around 0.28 nm, which is much smaller than that of Zr-Zr bond length (~ 0.32 nm).²⁾ Thus, the Cu-Cu distance may be ~ 0.453 ($= 0.28 \times 1.618$) nm in the case of the icosahedron structure (Fig. 3(d)), while it may be 0.485 ($= 0.28 \times 1.732$) nm for the hcp-structure (Fig. 3(c)). The former distance is just that for the strong Cu-Cu attraction ($0.45\sim 0.46$ nm) in Fig. 5(c) and the latter is between the distances of strong attraction ($0.45\sim 0.46$ nm) and strong repulsion (0.53 nm) in Fig. 5(d). Thus, we can easily expect that the $\text{Zr}_{10}\text{Cu}_3$ hcp-structure (Fig. 3(c)) is transformed to an icos-like $\text{Zr}_{10}\text{Cu}_3$ structure (Fig. 3(d)) by the strong Cu-Cu attraction (the energy gain of -0.1 eV per pair). This mechanism may be justified if the energy gain due to the 2nd-neighboring Cu-Cu interaction overcomes the energy loss due to the rearrangement of the surrounding Zr-Cu bonds. As discussed in 3.1, the Zr-Cu bond may be not strong because of the strong localization of Cu-3d orbitals. The small size of Cu atoms may also be important for the rearrangements of Cu atoms towards the 2nd-neighboring sites in an icos-like $\text{Zr}_{10}\text{Cu}_3$ structure.

It is noted that the Zr_9Cu_4 icos-like cluster, which is formed by replacing a Zr atom at the site (5) in the bottom layer of $\text{Zr}_{10}\text{Cu}_3$ (Fig. 6(a)) with a Cu atom may also be stabilized by the 2nd-neighboring Cu-Cu attraction because the replacement of a Zr with a Cu results in the increase of one 1st-neighboring Cu-Cu pair (repulsion of 0.11 eV) and two 2nd-neighboring Cu-Cu pairs (attraction of 0.13 eV). Meanwhile, replacing another Zr atom by a Cu atom in the

Fig. 4 Distance dependence (1st to 8th in Fig. 3(a)) of X-X (X = Sc-Cu, Y-Ag) interaction energies in Zr-fcc.

Zr_9Cu_4 cluster may cause an unstabilization by the dominant 1st neighboring Cu-Cu pair. Then we can predict the unstability of a Zr_8Cu_5 cluster in the BMG.

The Zr_9Cu_4 cluster is stoichiometrically close to the $Zr_{70}Cu_{30}$ BMG. However, it is known that there exist several additional atoms surrounding the icosahedral sites such as in quasicrystals. Thus both of the Zr_9Cu_4 and $Zr_{10}Cu_3$ clusters may exist in the $Zr_{70}Cu_{30}$ BMG.

Fig. 5 Distance dependence of X-X (X = Cu, Ni) interaction energies in Zr-fcc (1st to 8th in Fig. 3(a)) and Zr-hcp (1st to 8th in Fig. 3(b)). There exist two kinds of 1st and 4th neighbors in Zr-hcp ($\circ$ corresponds to 1 and 4, while $\times$ to 1' and 4' in Fig. 3(b)).

On the other hand, the Zr-Ni bond may be very strong because of the delocalization of Ni-3d orbital and the Friedel's band-filling, as discussed in 3.1. Thus, we can easily expect that the strong Zr-Ni bonds prevent the relaxation of three Ni atoms from the hcp-structure (Fig. 3(c)) toward an icos-like structure (Fig. 3(d)). In order to get the more information of the bond strength of X (X = Cu, Ni) with Zr, we studied the lattice relaxation effect around X in Zr. The lattice relaxation energy of Ni is large (~ -0.15 eV), compared with that (~ -0.11 eV) of Cu.¹⁶⁾ This result also supports that the Ni atom makes a strong bond with the nearest-neighboring Zr atoms, compared with Zr-Cu bond.

3.3 Atomic structure of isolated $Zr_{10}X_3$ clusters

In order to discuss the stable structure of $Zr_{10}Cu_3$ in the $Zr_{70}Cu_{30}$ BMG, we calculated the optimized structure of isolated $Zr_{10}X_3$ (X = Cu, Ni) clusters by using the STO-basis-set ab-initio calculations with the GGA and the TZP bases.¹⁴⁾

For X = Cu, we have found the stable structures shown in Figs. 6(a) and (b): the icos-like structure (Fig. 6(a)) is more stable by 0.68 eV than the hcp-like structure (Fig. 6(b)). The icos-like structure (Fig. 6(a)) is obtained by starting from an initial atomic structure of a small up-shift (~ 0.01 nm) of three Cu atoms in a hcp structure (Fig. 3(c)), while the hcp-like structure (Fig. 6(b)) only from just a hcp-structure of pure-Zr (Fig. 3(c)). It is noted that the Cu-Cu distance in the icos-like structure (Fig. 6(a)) is 0.465 nm, being close to the distance for the strong Cu-Cu attraction in Fig. 5(c), while the Cu-Cu distance in the hcp-structure (Fig. 6(b)) is

Fig. 6 Optimized atomic structures of isolated Zr_{10}X_3 ($\text{X} = \text{Cu}, \text{Ni}$) clusters: (a) icosahedron-like $\text{Zr}_{10}\text{Cu}_3$, (b) hcp-like $\text{Zr}_{10}\text{Cu}_3$, (c) hcp-like $\text{Zr}_{10}\text{Ni}_3$, and (d) icosahedron-like $\text{Zr}_{10}\text{Ni}_3$. The stable atomic structures are (a) for $\text{X} = \text{Cu}$ and (c) for $\text{X} = \text{Ni}$. See the text for details.

0.489 nm, being away from the distance of the strong Cu-Cu attraction.

For $\text{X} = \text{Ni}$, we have found the stable structures shown in Figs. 6(c) and (d): the hcp-like structure (Fig. 6(c)) is more stable by 0.23 eV than the icos-like structure (Fig. 6(d)). The hcp-like structure is obtained by starting a hcp structure, while the icos-like structure by starting only from an atomic structure close to an icosahedron structure. For these structures, the Ni-Ni distances are 0.482 nm (Fig. 6(c)) and 0.436 nm (Fig. 6(d)), all of which are away from the distance of Ni-Ni strong attraction. These results support that the stability of both the structures is not due to the Ni-Ni pair interaction, but due to the strong Zr-Ni bonds, as discussed in 3.1. The important is that the shape of a $\text{Zr}_{10}\text{Ni}_3$ cluster can be never transformed from a hcp structure (Fig. 6(c)) to an icos-like structure (Fig. 6(d)).

4. Summary and Future Problem

We have presented ab-initio data for Zr-rich ZrX ($\text{X} = \text{Sc-Cu}$) alloys and discussed the fundamental features of Zr-rich ZrX alloys. It was shown that the strong attraction of Cu-Cu around 0.45~0.46 nm is very important for the stability of icos-like local structures of $\text{Zr}_{10}\text{Cu}_3$ and Zr_9Cu_4 in the $\text{Zr}_{70}\text{Cu}_{30}$ BMG.

In order to establish the present mechanism for the stability of icos-like local structures in Zr-rich ZrCu alloys, we must perform the atomistic simulations¹⁷⁾ with the accurate interatomic potentials. Mishin *et al.* recently showed that the reliable embedded-atom-method potential (EAMP) can be developed by fitting to the ab-initio calculation results.¹⁸⁾ Following them, we are now constructing the reliable EAMP

of Zr-rich ZrCu alloys, all the parameters in which are determined by fitting to the present ab-initio data.

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