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*Invited Paper*

# Analyses of characteristics of atomic pairs in ferrous bulk metallic glasses using classification of bulk metallic glasses and pettifor map

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Characteristics of atomic pairs in ferrous bulk metallic glasses (BMGs) have statistically been analyzed using digitized data on mixing enthalpy ($\Delta H_{\{AB\}}^{mix}$) based on the Miedema's model and local atomic arrangements for binary compounds listed in Pettifor map. The main element of the ternary ferrous BMGs tend to be the element with intermediate atomic radius in a system, which is different from most of the other BMGs. The ternary ferrous BMGs exhibits strict restrictions with respect to $\Delta H_{\{AB\}}^{mix}$'s for the formation of ferrous BMGs. These tendency and restrictions are the necessity of multicomponent alloying for the formation of ferrous BMGs. The local atomic arrangements of BMGs were carried out for pseudo-binary systems in multicomponent BMGs by referring to the corresponding compositions in Pettiffor map with ratios of elements of 1:1, 2:1, 3:1, 4:3, 3:2 and 5:3. The analyses with respects to types of environment, coordination number, coordination notation and coordination symbol for binary compounds reveal the local atomic arrangements of BMGs containing a part of icosahedral clusters as a common basic atomic arrangements. This kind of statistical analyses using computers is useful for the further development of BMGs.

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*Keywords:* Mixing enthalpy, Local atomic arrangement, Bulk metallic glass, Miedema model, Pettifor map

## 1. Introduction

Recently, there has been great progress in the development of bulk metallic glasses (BMGs) due to great efforts for discovering new alloy compositions in Mg-, Lanthanide-, Zr-, Pd-Cu and Fe-based systems [1]. These BMGs are frequently fabricated by selecting the constituent elements with referring to the criteria for the achievement of high glass-forming ability: (1) multicomponent systems consisting of three or more elements, (2) significant atomic size mismatch greater than or equal to 12 %, and (3) negative heats of mixing. Here, it is noted that each criterion consists of quantity, denoted as number of elements (NOE), atomic size mismatch (ASM) or heats of mixing (HOM), and its threshold value. This notation enables us to describe the criteria mentioned above as (NOE, ASM, HOM) = ($\geq 3$, $\geq 12$, $<0$). Besides the BMGs, it is reported [2] that other non-equilibrium materials can be fabricated when another set of threshold value is applied for the quantities. For instance, nanocrystalline dispersed bulk metallic glasses can be fabricated when the following condition is satisfied (NOE, ASM, HOM) = ($\geq 3$, $\geq 7$, $<0$). From these results, it is of great importance to pay attention to the necessary quantities which control the formation of non-equilibrium materials.

In addition to the criteria mentioned above, Inoue succeeded in summarizing the classification of BMGs [3] in 2000. In this classification of BMGs, the characteristics of BMGs are focused on in terms of chemical spices and the atomic size mismatches, and the BMGs found until 2000 were classified into five groups. Sequentially, Takeuchi and Inoue [4] have recently improved the classification result by adding new BMGs found during 2000 to date. On the other hand, Jeevan and Ranganathan [5] carried out classification of quasicrystals with the Mendeleev number concept devised by Pettifor for drawing structure maps [6].

Among the BMGs found to date, there exists great difference in the maximum sample thickness for each type of BMGs. For instance, the maximum sample thickness of the ferrous BMGs is approximately several millimeters while it reaches to 72 mm for Pd-Cu-Ni-P BMGs [1]. This difference in the maximum sample thickness indicates the difficulty for the formation of ferrous BMGs. Thus, it is important to clarify the characteristics of the ferrous BMGs by paying attention to the necessary quantities for the formation of the ferrous BMGs, and by comparing the characteristics of the ferrous BMGs with those of the other BMGs.

The purpose of the present study is to clarify the characteristics of the atomic pairs in ferrous BMGs

with respects to the mixing enthalpy combined with the classification results of BMGs, and local atomic arrangements of BMGs.

## 2. Data used for the analyses

In the present study, characteristics of atomic pairs are analyzed statistically for the typical ferrous BMGs as well as the other BMGs found to date in terms of mixing enthalpy ($\Delta H^{mix}_{\{AB\}}$) based on the Miedema's semi-empirical model [7,8], classification of BMGs proposed by Takeuchi and Inoue [4] and local atomic arrangement based on the Pettifor map for binary compounds [9]. The details of the data are described below.

### *2.1 Ferrous BMGs*

Since the first synthesis of ferrous BMGs in Fe-based multicomponent system in 1995 [10], a number of ferrous BMGs have been fabricated sequentially. Table 1 summarizes the ferrous and non-ferrous BMGs, and calendar years when details about each alloy system were first published. Table 1 is tabulated on the basis of the previous data [11] until 2002.

*Table 1. Typical ferrous bulk amorphous alloy systems and calendar years when details about each alloy system were first published. The non-ferrous BMGs are also shown for comparison. The data up to 2002 are quoted from literature [11].*

| Ferrous Alloy system | Year | | Non-Ferrous Alloy system | Year |
|---|---|---|---|---|
| Fe–(Al, Ga)–(P, C, B, Si, Ge) | 1995 | | Mg–Ln–M (Ln: lanthanide metal; M: Ni, Cu, Zn) | 1988 |
| Fe–(Nb, Mo)–(Al, Ga)–(P, B, Si) | 1995 | | Ln–Al–TM (TM: Fe, Co, Ni, Cu) | 1989 |
| Co–(Al, Ga)–(P, B, Si) | 1996 | | Ln–Ga–TM | 1989 |
| Fe–(Zr, Hf, Nb)–B | 1996 | | Zr–Al–TM | 1990 |
| Co–(Zr, Hf, Nb)–B | 1996 | | Ti–Zr–TM | 1993 |
| Ni–(Zr, Hf, Nb)–B | 1996 | | Zr–Ti–TM–Be | 1993 |
| Fe–Co–Ln–B | 1998 | | Zr–(Ti, Nb, Pd)–Al–TM | 1995 |
| Fe–Ga–(Cr, Mo)–(P, C, B) | 1998 | | Pd–Cu–Ni–P | 1996 |
| Fe–(Nb, Cr, Mo)–(C, B) | 1999 | | Pd–Ni–Fe–P | 1996 |
| Ni–(Nb, Cr, Mo)–(P, B) | 1999 | | Pd–Cu–B–Si | 1997 |
| Co–Ta–B | 1999 | | Ti–Ni–Cu–Sn | 1998 |
| Fe–Ga–(P, B) | 2000 | | Cu–(Zr, Hf)–Ti | 2001 |
| Ni–Zr–Ti–Sn–Si | 2001 | | Cu–(Zr, Hf)–Ti–(Y, Be) | 2001 |
| Ni–(Nb, Ta)–Zr–Ti | 2002 | | Cu–(Zr, Hf)–Ti–(Fe, Co, Ni) | 2002 |
| Fe–Si–B–Nb | 2002 | | Ca-Mg-Zn [13] | 2004 |
| Co–Fe–Si–B–Nb | 2002 | | | |
| Ni–Si–B–Ta | 2002 | | | |
| Co-Fe-Ta-B [12] | 2004 | | | |

### *2.2 Mixing enthalpy*

Miedema's model [7,8] is an empirical calculation model which can deal with the changes in enthalpy at the interface of Wigner-Seitz cells, where the two different cells are in contact. The values of enthalpy are calculated with molar volume, work function and the density at the boundary of the cells. By using Miedema's model, one can calculate mixing enthalpy ($\Delta H^{mix}_{\{AB\}}$) for 2628 atomic pairs consisting of 73 elements of transition metal (TM) and non-transition metal (NTM). Lower-left part of Table 2 summarizes the values of $\Delta H^{mix}_{\{AB\}}$ in units of kJ/mol at an equiatomic composition for the atomic pairs consisting of elements listed in Table 2 and Pr, Nd and Sm for comparison. It should be noted that the values of $\Delta H^{mix}_{\{AB\}}$ containing NTM (H, B, C, N, P, Si and Ge) are modified [3] from the original values of $\Delta H^{mix}_{\{AB\}}$ [7,8] because of the subtraction term needed for NTMs to transform to metallic elements [7,8], where $\Delta H^{trans}_{i}$ (i= H, B, C, N, P, Si and Ge) are (100, 30, 180, 310, 17, 34 and 25) kJ/mol, respectively [7]. Since we consider the A-B system at the equi-atomic composition in a A-B binary system, the subtraction term is $\Delta H^{trans}_{i}/2$ for TM-NTM and $(\Delta H^{trans}_{i} + \Delta H^{trans}_{j})/2$ for NTM-NTM where i and j are the different elements ($i \neq j$) in NTMs. These modifications are required for the atomic pairs containing B, C, P, Si and Ge for the ferrous BMGs.

*Table 2. Mixing enthalpy ($\Delta H^{mix}_{\{AB\}}$) in units of kJ/mol at an equiatomic composition for the atomic pairs consisting of elements listed in Table 1, and Pr, Nd and Sm for comparison. The data for atomic size mismatch (Δr (%)) are also shown for comparison for the same atomic pairs to the $\Delta H^{mix}_{\{AB\}}$.*

| $\Delta H^{mix}_{\{AB\}}$ | r | 5 | 6 | 13 | 14 | 15 | 22 | 24 | 26 | 27 | 28 | 31 | 32 | 40 | 41 | 42 | 50 | 59 | 60 | 62 | 72 | 73 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | B | C | Al | Si | P | Ti | Cr | Fe | Co | Ni | Ga | Ge | Zr | Nb | Mo | Sn | Pr | Nd | Sm | Hf | Ta |
| 5 | B | | 15.6 | 45.5 | 26.1 | 19.1 | 48.1 | 32.6 | 31.8 | 32.6 | 32.6 | 31.8 | 31.0 | 57.1 | 45.5 | 40.7 | 44.2 | 68.1 | 67.6 | 66.2 | 56.0 | 45.5 |
| 6 | C | 95 | | 60.0 | 41.2 | 34.4 | 62.5 | 47.5 | 46.8 | 47.5 | 47.5 | 46.8 | 46.0 | 71.1 | 60.0 | 55.4 | 58.7 | 81.5 | 81.1 | 79.7 | 70.0 | 60.0 |
| 13 | Al | 15 | 54 | | 20.0 | 27.0 | 2.8 | 13.4 | 14.2 | 13.4 | 13.4 | 14.2 | 15.0 | 12.5 | 0.0 | -5.0 | -1.4 | 24.5 | 24.0 | 22.4 | 11.2 | 0.0 |
| 14 | Si | 18 | 68 | -2 | | 7.1 | 22.7 | 6.6 | 5.8 | 6.6 | 6.6 | 5.8 | 5.0 | 32.3 | 20.0 | 15.0 | 18.6 | 44.0 | 43.5 | 41.9 | 31.0 | 20.0 |
| 15 | P | 24 | 94 | -12 | 0 | | 29.7 | 13.7 | 12.9 | 13.7 | 13.7 | 12.9 | 12.1 | 39.1 | 27.0 | 22.0 | 25.6 | 50.7 | 50.2 | 48.6 | 37.9 | 27.0 |
| 22 | Ti | -43 | -19 | -30 | -49 | -92 | | 16.2 | 17.0 | 16.2 | 16.2 | 17.0 | 17.8 | 9.7 | 2.8 | 7.8 | 4.2 | 21.8 | 21.3 | 19.6 | 8.5 | 2.8 |
| 24 | Cr | -16 | 29 | -10 | -20 | -41 | -7 | | 0.8 | 0.0 | 0.0 | 0.8 | 1.6 | 25.8 | 13.4 | 8.4 | 12.0 | 37.7 | 37.1 | 35.5 | 24.6 | 13.4 |
| 26 | Fe | -11 | 40 | -11 | -18 | -31 | -17 | -1 | | 0.8 | 0.8 | 0.0 | 0.8 | 26.6 | 14.2 | 9.2 | 12.8 | 38.4 | 37.9 | 36.3 | 25.4 | 14.2 |
| 27 | Co | -9 | 48 | -19 | -21 | -27 | -28 | -4 | -1 | | 0.0 | 0.8 | 1.6 | 25.8 | 13.4 | 8.4 | 12.0 | 37.7 | 37.1 | 35.5 | 24.6 | 13.4 |
| 28 | Ni | -9 | 51 | -22 | -23 | -26 | -35 | -7 | -2 | 0 | | 0.8 | 1.6 | 25.8 | 13.4 | 8.4 | 12.0 | 37.7 | 37.1 | 35.5 | 24.6 | 13.4 |
| 31 | Ga | 21 | 57 | 1 | 0 | -10 | -23 | -1 | -2 | -11 | -15 | | 0.8 | 26.6 | 14.2 | 9.2 | 12.8 | 38.4 | 37.9 | 36.3 | 25.4 | 14.2 |
| 32 | Ge | 27 | 73 | -2 | 19 | 4 | -39 | -6 | -3 | -9 | -11 | -3 | | 27.4 | 15.0 | 10.0 | 13.6 | 39.2 | 38.7 | 37.1 | 26.1 | 15.0 |
| 40 | Zr | -56 | -41 | -44 | -67 | -119 | 0 | -12 | -25 | -41 | -49 | -40 | -60 | | 12.5 | 17.4 | 13.9 | 12.2 | 11.6 | 10.0 | 1.2 | 12.5 |
| 41 | Nb | -39 | -12 | -18 | -39 | -81 | 2 | -7 | -16 | -25 | -30 | -8 | -24 | 4 | | 5.0 | 1.4 | 24.5 | 24.0 | 22.4 | 11.2 | 0.0 |
| 42 | Mo | -19 | 23 | -5 | -18 | -45 | -4 | 0 | -2 | -5 | -7 | 7 | -1 | -6 | -6 | | 3.6 | 29.5 | 28.9 | 27.3 | 16.2 | 5.0 |
| 50 | Sn | 33 | 67 | 4 | 6 | 1 | -21 | 10 | 11 | 0 | -4 | 1 | 0 | -43 | -1 | 20 | | 25.9 | 25.4 | 23.8 | 12.6 | 1.4 |
| 59 | Pr | -34 | -27 | -38 | -56 | -104 | 17 | 13 | 1 | -20 | -30 | -41 | -60 | 10 | 32 | 26 | -52 | | 0.5 | 2.2 | 13.4 | 24.5 |
| 60 | Nd | -34 | -26 | -38 | -56 | -104 | 17 | 13 | 1 | -20 | -30 | -40 | -89 | 10 | 32 | 26 | -51 | 0 | | 1.7 | 12.9 | 24.0 |
| 62 | Sm | -35 | -27 | -38 | -57 | -105 | 15 | 11 | -1 | -22 | -31 | -40 | -60 | 9 | 30 | 24 | -51 | 0 | 0 | | 11.2 | 22.4 |
| 72 | Hf | -51 | -33 | -39 | -60 | -109 | 0 | -9 | -21 | -35 | -42 | -34 | -53 | 0 | 4 | -4 | -35 | 13 | 13 | 11 | | 11.2 |
| 73 | Ta | -39 | -11 | -19 | -39 | -81 | 1 | -7 | -15 | -24 | -29 | -10 | -25 | 3 | 0 | -5 | -3 | 29 | 29 | 27 | 3 | |

### *2.3 Classification of bulk metallic glasses*

On the basis of a previous classification result of BMGs proposed by Inoue [2], Takeuchi and Inoue [3] revised the classification of the BMGs found to date. As a result, the BMGs are classified into seven groups as shown in Fig. 1. (G-I) ETM/Ln-LTM/BM-Al/Ga, (G-II) ETM/Ln-LTM/BM-Metalloid, (G-III) Al/Ga-LTM/BM-Metalloid, (G-IV) IIA-ETM/Ln-LTM/BM, (G-V) LTM/BM-Metalloid, (G-VI) ETM/Ln-LTM/BM and (G-VII) IIA-LTM/BM where ETM, Ln, LTM, BM and IIA are the early transition metal, lanthanide metal, late transition metal, IIIB-IVB metal and the IIA-group metal, respectively. The characteristics of the main element of ternary BMGs are reported, and will be discussed in Section 3.

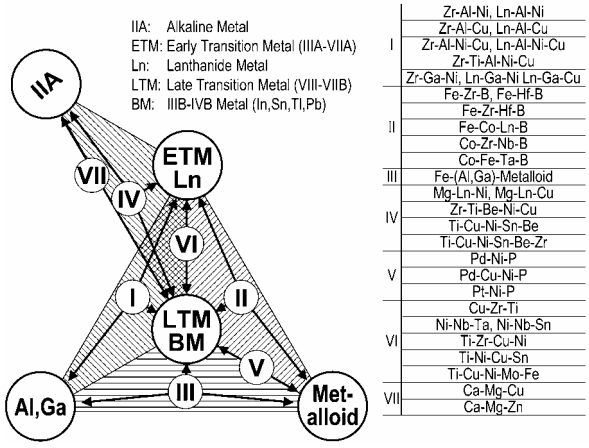



*Fig. 1. Seven groups of BMGs consisting of groups of elements (ETM/Ln, LTM/BM, Al,Ga, IIA and Metalloid) [4] modified from a previous result [3].*

### *2.4 Pettifor map*

The local atomic arrangements of BMGs were analyzed on the basis of those of the binary compounds listed in Pettifor map [9] in the following procedures. First, all the data of binary compounds of A-B system with a composition ratio of A:B or B:A = 1:1, 2:1, 3:1, 4:3, 3:2,5:3 are digitized and saved in a file of a spreadsheet software. Then, characteristics of BMGs were analyzed with respects to the following main terms. Types of environment (single-, two-, three- and four-environment types), Coordination number (CN), Coordination notation ($12^{2.2}$, $6^{5.0}3^{4.0}/9^{5.0}3^{6.0}1^{3.0}$, …) and Coordination symbol (p1, kP, …) which are dealt with in the literature [9]. These terms are treated as kinds of quantity for analyses in the present study. In order to obtain the quantities corresponding to a composition of BMG, multicomponent systems are described as the sums of psuedo-binary systems for the composition of BMG. For instance, $A_aB_bC_c$ ternary BMG (constituent elements A, B and C and compositions a, b and c) are described as the sum of the following three psuedo-binary systems: $A_{a/(a+b)}B_{b/(a+b)}$, $B_{b/(b+c)}C_{c/(b+c)}$, $C_{c/(c+a)}A_{a/(c+a)}$. In a similar manner, multicomponent BMGs are also described as the sum of the psuedo-binary systems. The local atomic arrangements of which a composition is described in the above psuedo-binary systems are referred to those of the composition ratio of 1:1, 2:1, 3:1, 4:3, 3:2,5:3.

### *2.5 Atomic radius*

The values of atomic radius are quoted form a databook. The validity of the data was confirmed by comparing the data with those listed in another databook. We use data from a databook [14] instead of the other one [15] because of a wide applicability of data for the elements of the BMG formers. For comparison, the atomic size mismatch ($\Delta r$) is tabulated in upper-right side of Table 2, although it is not directly discussed in the present study. The $\Delta r$ is calculated with $\Delta r = |2\cdot(r_a-r_b)/(r_a+r_b)|$, where $r_a$ and $r_b$ denote atomic radius of A and B atoms, respectively.

## 3. Results and discussion

### *3.1 Characteristics of the main element in ferrous BMGs*

Fig. 2 shows characteristics of BMGs with respects to atomic size mismatch and $\Delta H^{\mathrm{mix}}_{\{AB\}}$. Figure 2 is drawn on the previous result [4], and is in particular emphasized for the ferrous BMGs.

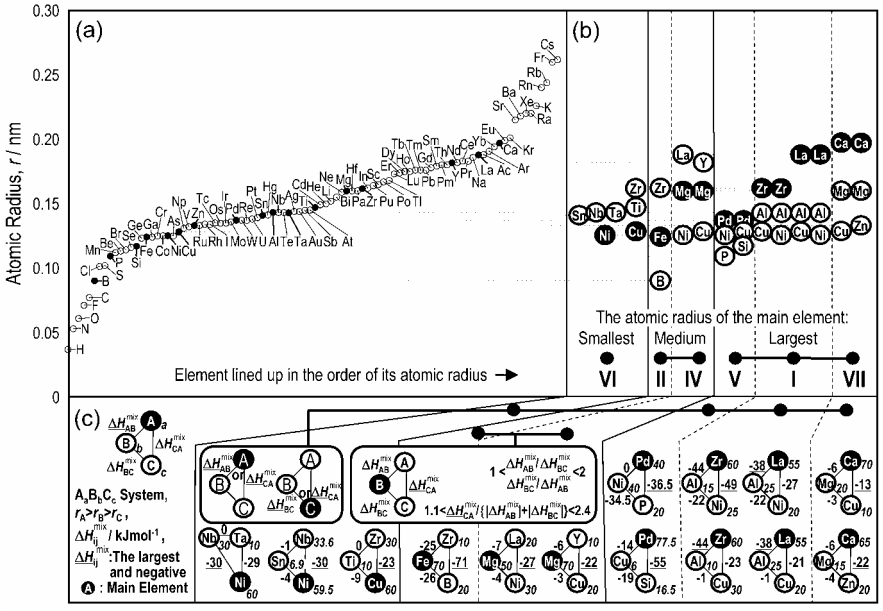



*Fig. 2. The relationships between the atomic size mismatch and $\Delta H^{\mathrm{mix}}_{\{AB\}}$ of the atomic pairs of BMGs. (a) The atomic radius of elements plotted in sequence of their atomic radii from smallest (H) to largest (Cs). (b) The atomic size mismatch among the constituent elements of representative ternary BMGs for the seven groups. The main elements are drawn in solid circles in which the symbol of the element is written in white. (c) The relationships of the $\Delta H^{\mathrm{mix}}_{\{AB\}}$ and typical composition for the ternary BMGs. The largest, negative values of $\Delta H^{\mathrm{mix}}_{\{AB\}}$ are underlined and the composition of the system is written in italics.*

In Fig. 2 (a), atomic radii of elements are plotted in sequence from the smallest (H) to the largest (Cs) so as to avoid overlapping of each element for the horizontal axis. Figure 2 (b) is obtained by tracing the atomic radii of elements from Fig. 2 (a) for the constituent elements of typical ternary BMGs, and solute elements for ferrous BMGs. Fig. 2 (c) summarizes the characteristics of $\Delta H_{\{AB\}}^{mix}$'s in ternary BMGs. In Figs. 2 (b) and (c), the main elements are drawn in solid circles in which the symbol of the element are written in white. The main alloying element of ternary G-I, G-V and G-VII, ternary G-II and G-IV, and ternary G-VI BMGs tends to be the largest, intermediate and smallest atomic radius compared to the other alloying elements, respectively. This tendency indicates disadvantages for the fabrication of ferrous BMGs due to the location of atomic radius of ferrous-group elements (Fe, Ni, Co) and restrictions with respects to $\Delta H_{\{AB\}}^{mix}$. That is, it is apparent that the atomic radius of Fe, Co and Ni locates at the smaller size region in whole the ranges in Fig. 2 (a), which reduces the numbers of candidate solute elements among the whole elements. In addition, for the formation of ferrous BMGs, there exists strict restrictions with respect to $\Delta H_{\{AB\}}^{mix}$ about the ratios and ranges of $\Delta H_{\{AB\}}^{mix}$, which are shown in Fig. 2 (c). Presumably, these restrictions also reduce the numbers of alloy systems to be formed as ferrous BMGs compared to those of the other BMGs. The tendency and restrictions of ferrous BMGs are interpreted the necessity of multicomponent alloying for the formation of ferrous BMGs in which as many as six or more constituent elements is required. Similar to ferrous BMGs, Mg-Cu-Y BMG which belongs to G-VI exhibits the similar tendency with respects to the main element and $\Delta H_{\{AB\}}^{mix}$'s of the constituent elements. However, the atomic radius of Mg locates at the middle region in whole the ranges in Fig. 2 (a), thus, the restrictions for the formation of BMGs are not rigid as the ferrous BMGs. These tendencies and restrictions are presumably reflected by the maximum sample thickness of BMGs reported previously [1] that maximum sample thickness of Mg- and Fe-based BMGs are approximately 10 and 6 mm, respectively [1].

### *3.2 Characteristics of the local atomic arrangements of ferrous BMGs*

Table 2 shows a part of the list used for the analyses of local atomic arrangements by Pettifor map. The analyses for all the ratios of compounds reveal that the following coordination symbols are frequently found in the typical BMGs: p3, p9, q3, PhL, kU, ms, mx, mx1, rv, rO, ry, ry2, ry3, jS and kP. In particular, coordination symbols of x and m are frequently seen in the ferrous BMGs. The common characteristics for the typical BMGs about the coordination symbols are summarized as follows: (1) polygonal structure in which some corners adjoining 5 triangles, no square (n5.0: n=4, 6, 8,…) and (2) icosahedral polygonal structure or its deformed structure ($12^{2.2}$). These features indicate that typical BMGs contain icosahedral clusters in their local structure.

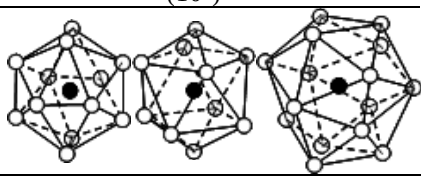
*Table 2. A part of the data used for the analyses of local atomic arrangements by Pettifor map. Table 2 consists of alloy and its constituent elements (A, B, C and D where the atomic size of the constituent elements are in this order), and coordination symbol for binary, ternary and quaternary amorphous/glassy alloys (A-B, A-B-C, A-B-C-D) for compounds with a ratio of 2:1. Similar table are also prepared for a ratio of 2:1 and other sets of ratios of 1:1, 3:1, 4:3, 3:2 and 5:3 with spreadsheet software. All the notations are from the literature [9]. Typical amorphous alloys quoted from a literature [16] are also shown for comparison.*

| Alloy | A | B | C | D | Coordination symbol | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | A2B | B2C | C2A | A2D | B2D | C2D |
| *$Fe_{83}B_{17}$ | Fe | B | | | mx1(2) | | | | | |
| *$Co_{75}Si_{15}B_{10}$ | Co | Si | B | | ms(2) | Vil | - | | | |
| *$Fe_{79}Si_{10}B_{11}$ | Fe | Si | B | | w4 w5(1) | Vil | kz1(2) | | | |
| *$Fe_{80}P_{13}C_7$ | Fe | P | C | | (P)ms(2) kr(3) | Mie | Vil | | | |
| *$Ni_{75}Si_8B_{17}$ | Ni | Si | B | | ms(2) 386 | Vil | - | | | |
| $Zr_{60}Al_{15}Ni_{25}$ | Zr | Al | Ni | | nu mx1(2) | - | ry3(2) | | | |
| $La_{60}Al_{15}Ni_{25}$ | La | Al | Ni | | - | - | ry3(2) | | | |
| $Ca_{70}Mg_{20}Cu_{10}$ | Ca | Mg | Cu | | - | mx(2) | - | | | |
| $Pd_{40}Ni_{40}P_{20}$ | Pd | Ni | P | | Nul | 405 kr(3) | 80 | | | |
| $Zr_{30}Ti_{10}Cu_{60}$ | Zr | Ti | Cu | | Nul | w3(1) | - | | | |
| $Y_{10}Mg_{70}Cu_{20}$ | Y | Mg | Cu | | - | mx(2) | mV(2) | | | |
| $Zr_{10}Fe_{70}B_{20}$ | Zr | Fe | B | | mx1 rQ(2) | mx1(2) | kz1(2) | | | |
| $Pd_{40}Cu_{30}Ni_{10}P_{20}$ | Pd | Cu | Ni | P | Nul | Nul | Nul | - | - | 405 kr(3) |
| $Zr_{55}Al_{15}Cu_{20}Ni_{10}$ | Zr | Al | Cu | Ni | nu mx1(2) | mx1(2) | - | mx1(2) | - | Nul |

** Alloy systems quoted from literature [16]. (1),(2),(3),(4): single-, two-, three- or four-environment types. Vil, Mie, and Nul: non-existence of a compound predicted by Villars, by enthalpy estimates of Miedema and co-workers, and by both, respectively. (P): High pressure phase. -: no information [9].*

On the other hand, the peculiar characteristics of the ferrous BMGs are summarized in Table 3 which shows the coordination number, coordination notation and coordination polyhedron for coordination symbol of r, m and x. In Table 3, type r exhibits exactly the icosahedral clusters while types of m and x, which is frequently seen in ferrous BMGs, are not the icosahedral clusters. However, the coordination notations of type m and x contains the five triangles in their elements in polyhedrons. For instance, $8^{5.0}$ in $8^{5.0}2^{4.0}$ ($10^{I}$) (type m) and $12^{5.0}$ in $12^{5.0}3^{6.0}$ (15) (type x) are a part of the $12^{5.0}$ ($10^{II}$), thus, one can presume that there are similarity in the types among r, m and x.

*Table 3. Coordination number, coordination notation and coordination polyhedron for coordination symbol of r, m and x. The implication of coordination notation is exemplified as follows [9]. $4^{3.0}$: 4 corners adjoining 3 triangles, no square.*

| Coordination symbol | r | m | x |
|---|---|---|---|
| Coordination number | 12 | 8 | 15 |
| Coordination notation | $12^{5.0}$ ($12^{II}$) | $8^{5.0}2^{4.0}$ ($10^{I}$) | $12^{5.0}3^{6.0}$ (15) |
| Coordination polyhedron |  | | |

## 4. Conclusions

Characteristics of atomic pairs in ferrous bulk metallic glasses (BMGs) have statistically been analyzed by comparing with those of the other BMGs in terms of mixing enthalpy ( $\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$ ) and local atomic arrangements. The following are the main results obtained from the present study.

1. The difficulty for obtaining ferrous BMGs results from the following characteristics of the ferrous BMGs. (1) The main alloying element (Fe, Co and Ni) of the ternary ferrous BMG in the element with the intermediate atomic radius, (2) the atomic radius of the ferrous elements locates at the smaller size region in whole the ranges of atomic radius of elements, and (3) rigid restrictions with respect to $\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$ for the formation of ferrous BMGs.

2. The common characteristics of the local atomic arrangements of BMGs are analyzed as follows (1) polygonal structure in which some corners adjoining 5 triangles, no square ($n^{5.0}$: n = 4, 6, 8,…), (2) icosahedral polygonal structure or its deformed structure ($12^{2.2}$). These results indicate that BMGs contains a part of icosahedral clusters in their local structure.

## References


[1] A. Inoue, Bulk Amorphous Alloys, Preparation and Fundamental Characteristics, Materials Science Foundations **4,** Eds. M. Magini and F.H. Wöhlbier, Trans Tech Publications, Netherlands (1998).

[2] A. Inoue, A. Takeuchi, Proc. 3rd Int'l Conf. on Slow Dynamics in Complex Systems, Sendai, p. 547 (2004).

[3] A. Inoue, Acta Mater. **48**, 279 (2000).

[4] A. Takeuchi, A. Inoue, Mater. Trans. **46** 2817 (2005).

[5] H. S. Jeevan, S. Ranganathan, J. Non-Cryst. Solids, **334,** 184 (2004).

[6] D. G. Pettifor, Mater. Sci. Tech. **4,** 675 (1988).

[7] F. R. de Boor, R. Boom, W. C. M. Mattens, A. R. Miedema, A. K. Nissen, Cohesion in Metals, ed. F. R. Boer and D. G. Perrifor, Elsevier Science Publishers B.V. (1988).

[8] H. Bakker, Enthalpies in Alloy: Miedema's Semi-Empirical Model, Materials Science Foundations **1**, Eds. M. Magini and F.H. Wöhlbier, Trans Tech Publications, Netherlands (1998).

[9] Structure of Binary Compounds, Eds. F.R. de Boer and D.G. Pettifor, Elsevier Science Publishers B.V., 1989, North Holland (1989).

[10] A. Inoue, Y. Shinohara, J. S. Gook, Mater. Trans., JIM, **36,** 1427 (1995).

[11] A. Inoue, A. Takeuchi: Mater. Sci. Eng., **A375-377** 16 (2004).

[12] A. Inoue, B. L. Shen, H. Koshiba, H. Kato, A. R. Yavari, Acta Mater. **52,** 1631 (2004).

[13] E. S. Park, D. H. Kim: J. Mater. Res. **19,** 685 (2004).

[14] Metal Databook, 4th edition, Japan Institute of Metal, Maruzen, p. 8 (2004) (in Japanese).

[15] Smithells Metals Reference Book, 8th edition, eds. W. F. Gale and T. C. Totemeier, Butterworth Heinemann Ltd., Netherlands (2003).

[16] H. A. Davies, Rapid quenching and formation of metallic glasses, in: B. Cantor (Ed.), Rapidly Quenched Metals, **Vol. 1**, Part III, The Metal Society, p. 1 (1978).



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