A cluster line approach for composition rules of quasicrystals and bulk metallic glasses

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Abstract. This paper analyzes the structure and composition characteristics of ternary quasicrystals and bulk metallic glasses from the viewpoint of atomic clusters. It is pointed out that quasicrystals and bulk metallic glasses satisfy a cluster line rule. The cluster line refers to a straight composition line linking a specific cluster to the third element in a ternary alloy phase diagram. A ternary quasicrystal or bulk metallic glass composition is located at the intersection point of two cluster lines. Ternary quasicrystal and bulk metallic glass compositions can be the expressed with a cluster-plus-glue-atom model which can predict new ternary bulk metallic glasses.

1. Introduction
Quasicrystals (QCs) and metallic glasses contain short-range orders characterized by spherical periodicity [1, 2]. Then their structures can be described by shelled structures, or atomic clusters with different shells. In our previous researches on QCs and bulk metallic glasses (BMGs), we have revealed an atomic cluster line phenomenon in ternary QC- and BMG-forming systems that could serve a practical criterion for composition design [3-6]. The atomic cluster line, or more simply the cluster line, refers to a straight composition line linking a specific atomic cluster composition to the third element in a ternary alloy phase diagram, that is to say, the third element serves as glue atoms linking atomic clusters. Here the atomic clusters are the 1st-shell polyhedra with certain coordination number (CN) in the local structure of crystalline phases. To illustrate how the cluster line is defined, we take the example of Zr6Al2Ni, a primary devitrification phase of many Zr-based BMGs.

This phase has the hexagonal InMg2 type structure (figure 1) that contains two separate binary CN11 trigonal prism clusters, one being binary Ni-Zr centered by Ni (Ni3Zr5) and the other being binary Al-Zr centered by Al (Al5Zr5). This cluster separation can be understood from the viewpoint of the enthalpies of mixing between the constituents, as follows. \( \Delta H_{Zr-Al} = -44 \) kJ/mol and \( \Delta H_{Zr-Ni} = -49 \) kJ/mol. These are each negatively much larger than \( \Delta H_{Al-Ni} = -22 \) kJ/mol [7], so that the separated Ni-Zr and Al-Zr atomic clusters are favored in the Zr-rich region. As can be seen from this figure, the smaller atoms, Al and Ni, are at the centers of Al5Zr5 and Ni3Zr5 trigonal prisms, respectively. Each prism can be subdivided into a CN6 trigonal prism, a CN9 side-capped trigonal prism and a CN11 capped trigonal prism. The binary clusters and their compositions are plotted in the ternary phase.
diagram in figure 1. The phase composition Al$_2$NiZr$_6$ is exactly located at the intersection of straight composition lines Al$_2$Zr$_9$-Ni and NiZr$_6$-Al. These two composition lines, termed cluster lines, extend from the binary clusters Al$_2$Zr$_9$ and NiZr$_6$, and point toward their respective third elements.

![Figure 1. Schematic composition chart of Zr-Al-Ni ternary system and a projected Zr$_6$Al$_2$Ni structure.](image)

The cluster line rule also gives insight into the structure of the ternary phase: Al$_2$NiZr$_6$ can be described either as the cluster NiZr$_6$, plus glue atoms of Al, or as the cluster Al$_2$Zr$_9$, plus glue atoms of Ni, Al$_2$NiZr$_6$ = (NiZr$_6$)Al$_2$ = (Al$_2$Zr$_9$)Ni$	ext{1.5}$. This cluster-plus-glue-atom model is a new way of understanding ternary alloy phase structures.

Since the cluster lines are originated from negative enthalpies of mixing of constituent elements, both the cluster line rule and the cluster-plus-glue-atom model should be general phenomena in other types of alloy phases as well. In the present paper, we will decipher the structures of QCs and BMGs from the viewpoint of their 1$^{st}$-shell atomic clusters and summarize the general feature of the cluster lines in QC- and BMG-forming systems. The key issue in applying the approach is the determination of the right clusters for the cluster lines. We will see that QCs and BMGs are characterized by basically four types of clusters centered by a small atom: CN12 icosahedron, CN12 pentagonal prism, CN10 Archimedes octahedral anti-prism, and CN11 (CN9 if only side-capped) trigonal prisms.

2. Cluster line in QC-forming systems

2.1. Al-based ternary QCs

Stable QCs are generally obtained in ternary alloy systems with strong composition-sensitivity [8], especially in ternary Al-rich systems [9, 10]. We comprehensively surveyed the composition characteristics of all stable Al-based ternary QCs in Al-(Cu, Pd, Ni)-TM (TM=Fe, Co, Cr, Mn, Rh, Ru, Re) from the viewpoint of the cluster lines [3, 4]. The constituent elements of these ternary QC-
forming systems are characterized generally by negative enthalpies of mixing (\(-\Delta H\)) and large atomic size differences. Negative enthalpies of mixing imply a tendency to form clusters consisting of dissimilar atoms, and large atomic size differences favor topological dense-packed clusters. All the Al-based ternary experimental QC compositions can be explained by appropriate cluster lines. That is to say, a ternary experimental QC composition is located at the intersection point of two cluster lines, one being an icosahedral cluster line. The other cluster line involves a CN10 capped Archimedean antiprism, a CN9 side-capped trigonal prism, a CN12 icosahedron, or a CN12 pentagonal prism.

Figure 2. Schematic composition chart of Al-Cu-Fe system. Icosahedral QC is related to dense-packed icosahedron \(\text{Al}_{10.7}\text{Fe}_2\) and Archimedean capped octahedral antiprism \(\text{Al}_8\text{Cu}_3\).

Here, we take the ternary Al-Cu-Fe QC-forming system for instance. The enthalpies of mixing between constitute elements are respectively \(\Delta H_{\text{Al-Fe}} = -11 \text{ kJ/mol}, \Delta H_{\text{Al-Cu}} = -1 \text{ kJ/mol} \) and \(\Delta H_{\text{Cu-Fe}} = 13 \text{ kJ/mol} \) [7], which favors separate Al-Fe and Al-Cu clustering. Al-Fe forms a decagonal quasicrystal over a large composition range and the main crystalline approximant is \(\text{Al}_{13}\text{Fe}_4\). The structural analysis indicates that a dense-packed icosahedral cluster \(\text{Al}_{10.7}\text{Fe}_2\) centered by Fe atom exists in the local structure of the \(\text{Al}_{13}\text{Fe}_4\) phase. The calculation of topologically dense-packing efficiency is as follows. The Goldschmidt atomic radii of Al and Fe being 0.143 nm and 0.127 nm respectively, the average atomic radius \(R_1\) of the 1st-shell atoms \(\text{Al}_{10.7}\text{Fe}_2\) is \(R_1 = 0.1416 \text{ nm}\), and the atomic radius ratio of the central Fe (\(R_0\)) over that of the 1st-shell atoms is \(R_{0/1} = R_0/R_1 = 0.897\). Then, the dense-packing efficiency, characterized with the difference \(\Delta\) between the real \(R_{0/1}\) value and the ideal ratio \(R^*\) value (\(R^*_{\text{CN12}}=0.902\)) of a cluster with 12 coordination number [11], is \(\Delta = (R_{0/1} - R^*) / R^* = -0.5 \%\), showing that this icosahedron is nearly ideally dense-packed. In Al-Cu, the only Al-rich phase \(\text{Al}_2\text{Cu}\) contains a CN10 capped Archimedean antiprism \(\text{Al}_8\text{Cu}_3\) centered by Cu with \(\Delta = 14.4 \%\) (\(R_{0/1} = 0.128 \text{ nm}, R^*_{\text{CN10}}=0.799\)) so that this is not a dense-packed cluster. Two cluster lines \(\text{Al}_{10.7}\text{Fe}_2\text{Cu}\) and \(\text{Al}_8\text{Cu}_3\text{Fe}\) are then constructed by linking \(\text{Al}_{10.7}\text{Fe}_2\) with Cu and \(\text{Al}_8\text{Cu}_3\) with Fe respectively, as shown in figure 2. They intersect at \(\text{Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13}\), very close to the experimental icosahedral QC composition \(\text{Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13}\) [12]. This intersection composition can be decomposed into a dense-packed icosahedron \(\text{Al}_{10.7}\text{Fe}_2\) plus four glue atoms Cu, i. e., \(\text{Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13} = (\text{Al}_{10.7}\text{Fe}_2)_4\text{Cu}_4\).
2.2. Ti-Zr-Ni ternary QCs

Compared with the Al-based QCs, the Ti-Zr-Ni ternary meta-stable QCs form within a line composition zone [13, 14, 15]. Recently, we reinvestigated this system and found that QCs can be formed at five intersection points of different cluster lines, as shown in figure 3. There exist only one Ti-rich cluster, a dense-packed icosahedral cluster Ti$_9$Ni$_4$ ($\Delta = -1.5 \%$, $R_{\text{Ti}} = 0.146$ nm, $R_{\text{Ni}} = 0.125$ nm) centered by a Ni atom, in the local structure of the fcc-Ti$_2$Ni phase. Two Ni-Zr Ni-centered clusters can be identified in Ni-Zr phases, including icosahedral cluster Zr$_9$Ni$_4$ ($\Delta = -8.4 \%$, $R_{\text{Zr}} = 0.160$ nm) and capped Archimedean antiprism Zr$_8$Ni$_3$ ($\Delta = 2.3 \%$). In addition, a ternary Ni-centered icosahedral cluster Ti$_{15.9}$Zr$_{6.1}$Ni ($\Delta = -9.5 \%$) is derived from the W-TiZrNi approximant phase. The cluster lines Ti$_9$Ni$_4$-Zr, Zr$_9$Ni$_4$-Ti, Zr$_8$Ni$_3$-Ti and Ti$_{15.9}$Zr$_{6.1}$Ni-Ni are then constructed. All the intersection points of the cluster lines are QC-forming compositions (figure 3).

![Figure 3. Schematic composition chart of Ti-Zr-Ni system. The clusters and cluster lines are labelled.](image)

3. Cluster lines in BMG-forming systems

Like QCs, BMGs with large glass-forming abilities (GFAs) are also multi-component alloy phases [16] and have close structural connections with QCs, particularly in some Zr-based systems with extremely high glass-forming abilities where primary devitrification phases are often quasicrystalline [17]. Such an observation reflects the fact that icosahedral short-range orders are widely present in amorphous alloys [18, 19].

Many experimental results [3, 5, 6, 20-22] corroborate that the cluster line approach is quite effective in determining the optimum glass forming compositions in ternary systems, including Cu-based, Zr-based, Y-based, Sm-based, Fe-based and Co-based alloy systems. In the following, we will present the cluster line characteristics in these BMG-forming systems.
3.1. Cu-Zr-M (M=Al, Ag, Ti, Nb, Ta, Mo)

A new series of Cu-based Cu-Zr-M (M=Al, Ag, Ti, Nb, Ta, Mo) ternary BMGs have been developed using the cluster line approach [5, 6]. These BMGs are all based on a binary Cu-centered icosahedral cluster $\text{Cu}_8\text{Zr}_5$ that exists in the local structure of the Cu-Zr$_3$ crystalline phase. This icosahedral cluster $\text{Cu}_8\text{Zr}_5$ is packed quite efficiently with $\Delta = 0.4\%$, and the $\text{Cu}_8\text{Zr}_5$-M cluster line is then constructed in Cu-Zr-M ternary systems (Fig. 4). Furthermore, the existence of the $\text{Cu}_8\text{Zr}_5$-type short-range order in Cu-Zr binary amorphous alloys was supported by EXAFS results [19).

**Figure 4.** Schematic composition chart of Cu-Zr-M (M=Al, Ag, Ti, Nb, Ta, Mo) ternary systems.

These Cu-Zr-M BMG compositions are quite close to the Cu-Zr edge and BMGs can be classified into two groups. One is expressed by the cluster-plus-glue atom model consisting of one $\text{Cu}_8\text{Zr}_5$ icosahedral cluster plus one M atom. That is to say, the experimental optimum BMG compositions are located on the $\text{Cu}_8\text{Zr}_5$-M (M=Al, Ag, Ti, Cu) cluster lines and are all approximately expressed with the formula \((\text{Cu}_8\text{Zr}_5)_1\text{M}_{1-x}\text{Cu}_x = \text{Cu}_{8+x}\text{Zr}_{5-x}\). This is supported by the efficient cluster packing proposed by Miracle [23]: dense-packed clusters centered by primary solute atoms are packed in a close-packing face-centered cubic like structure and the secondary solute atoms (or glue atoms as we call them) are located in the interstitial sites, especially in the octahedral sites. For an fcc structure, the ratio of the number of atoms to that of octahedral interstices is 1:1, which coincides exactly with the above BMG composition formula \((\text{Cu}_8\text{Zr}_5)_1\text{M}_{1-x}\text{Cu}_x\). This binary BMG can be expressed with a $\text{Cu}_8\text{Zr}_5$ cluster plus a Cu atom, $(\text{Cu}_8\text{Zr}_5)\text{Cu} = \text{Cu}_\text{Cu}_8\text{Zr}_5 = \text{Cu}_{8+1}\text{Zr}_{5-1}$. Thus, the minor-alloyed ternary BMG compositions are located along a $\text{Cu}_\text{Cu}_8\text{Zr}_5$-M composition line (figure 4) and the BMG compositions are expressed with formula \([(\text{Cu}_8\text{Zr}_5)](\text{Cu},\text{M})_x \approx (\text{Cu}_8\text{Zr}_5)_{1-x}\text{M}_x\), i.e. Cu and M both serve the glue atoms. This may explain the mechanism of minor alloying effect [25] commonly encountered in BMG forming alloys.
3.2. Zr-Al-Ni (Co)
These two systems are typical Zr-based ternary BMGs. The strong interactions (strong negative enthalpies of mixing) between Zr and Ni (or Al) favor the Zr-Ni and Zr-Al dissimilar atom clustering. An example of the Al\textsubscript{2}NiZr\textsubscript{6} phase in this system has been shown in figure 1, where indeed the ternary structure is divided into two binary substructures Ni-Zr and Al-Zr, both being two CN9/CN11 capped trigonal prisms. Therefore, the reported composition Zr\textsubscript{60}Al\textsubscript{20}Ni\textsubscript{20} [26] can be easily understood via CN11 capped trigonal prism cluster lines Zr\textsubscript{9}Al\textsubscript{3}-Ni and Zr\textsubscript{9}Ni\textsubscript{3}-Al, as shown in figure 1, where the packing ratios of Zr\textsubscript{9}Al\textsubscript{3} and Zr\textsubscript{9}Ni\textsubscript{3} are respectively \( \Delta = 3.1 \% \) and -8 \% \( (R^{*}_{CN11}=0.884) \). The cluster lines give the interception composition Zr\textsubscript{60}Al\textsubscript{20}Ni\textsubscript{20} = (Zr\textsubscript{9}Al\textsubscript{3})Ni\textsubscript{3}, one dense-packed Zr\textsubscript{9}Al\textsubscript{3} cluster plus three Ni glue atoms. Another intersection composition Zr\textsubscript{57.2}Al\textsubscript{21.4}Ni\textsubscript{21.4} (figure 1) of two CN10 capped Archimedean antiprisms cluster lines Zr\textsubscript{8}Ni\textsubscript{3}-Al and Zr\textsubscript{8}Al\textsubscript{3}-Ni has also a large GFA, similar to Zr\textsubscript{60}Al\textsubscript{20}Ni\textsubscript{20}. The Zr\textsubscript{8}Ni\textsubscript{3} cluster is dense-packing with \( \Delta = 2 \% \), while Zr\textsubscript{8}Al\textsubscript{3} cluster is relatively loose \( (\Delta = 14.3 \%) \). This BMG composition Zr\textsubscript{57.2}Al\textsubscript{21.4}Ni\textsubscript{21.4} is composed of one Zr\textsubscript{8}Ni\textsubscript{3} cluster plus three Al glue atoms (Zr\textsubscript{8}Ni\textsubscript{3})Al\textsubscript{3}. In addition, the composition BMG Zr\textsubscript{53}Al\textsubscript{25}Ni\textsubscript{22.5} [20] was found to have the largest GFA along the icosahedral Zr\textsubscript{9}Ni\textsubscript{4}-Al cluster line, but its GFA is still slightly inferior to those of Zr\textsubscript{60}Al\textsubscript{20}Ni\textsubscript{20} and Zr\textsubscript{57.2}Al\textsubscript{21.4}Ni\textsubscript{21.4}.

It is noted that these best glass-forming compositions are all located on another composition line with \( e/a=1.5 \) [27], as shown in figure 1. This is actually our \( e/a \)-constant criterion, where \( e/a \) is the electron concentration of an alloy defined with \( e/a=\Sigma C_i (e/a)_i \), \( C_i \) and \( (e/a)_i \) being respectively the atomic fraction and effective electron contribution of the \( i \)th element. The effective electron contributions of Zr, Al, Ni are respectively +1.5, +3 and 0 [27].

![Figure 5](image)

**Figure 5.** Schematic composition chart of Y-Al-Ni/Co ternary system.

3.3. Y-Al-Ni (Co)
The BMG formation in Y-Al-Ni and Y-Al-Co systems is extremely composition sensitive and the composition range is very narrow [21]. The atomic radius of Y is 0.18 nm and the large difference in atomic size between Y and Ni/Co makes the capped trigonal prism Y\textsubscript{7}Ni(Co)\textsubscript{3} topologically dense-packed, \( \Delta = 5 \% \). In addition, there exists an \( e/a \)-constant line with \( e/a=1.5 \), where the effective electron contribution of Y is taken as +1.5 [21]. The dense packing cluster line Y\textsubscript{7}Ni(Co)\textsubscript{3}-Al and the \( e/a-\)
constant line intersect at the optimum BMG composition Y_{54}Al_{23}Ni(Co)_{23}, as shown in figure 5, which can also be described by the one Y_{7}Ni(Co)_{3} cluster glued with three Al atoms [Y_{7}Ni(Co)_{3}]_{1}Al_{3}.

3.4. Sm-Al-Co (Ni)

After an analysis of the local structures of crystalline phases in Sm-Al-Co system, we find no suitable binary clusters but instead two dense-packed ternary clusters, a CN10 Archimedean antiprism Sm_{6}Al_{3}Co_{2} centered by Co (Δ = -4.3 %, R_{Sm}=0.18 nm, R_{Co}=0.125 nm,) and an icosahedron Sm_{6}AlCo_{4} centered by Al (Δ = -1.9 %). Cluster lines are defined by linking these two ternary clusters to the third element respectively and they intersect at the best BMG composition Sm_{50}Al_{25}Co_{25} [22], as shown in figure 6, which is described with the cluster-plus-glue atom model as Sm_{50}Al_{25}Co_{25} = (Sm_{6}Al_{3}Co_{2})_{1}Co_{1} = (Sm_{8}AlCo_{4})_{1}Al_{3}. Moreover, the BMGs in this system are composition-sensitive and the BMG-forming range is less than 6 atomic percents.

**Figure 6.** Schematic composition chart of Sm-Al-Co ternary system.

3.5. TM-based (TM=Fe or Co) multi-component systems

The TM-based BMG formations in multi-component alloy systems are carried out by a combination of cluster line and minor-alloying principle [25]. Both Fe-B and Co-B form the most dense-packed CN10 Archimedean antiprism Fe_{8}B_{3} (Δ = 1.2 %, R_{Fe}=0.098 nm) and Co_{8}B_{3} (Δ = 2.5 %) centered by B atom. Take the Co-B-Si-Nb quaternary system for instance [28], which is first reported on BMG formation in this system. The Co-B-Si ternary system is determined first to be the basic system, and the enthalpies of mixing of Co-B, Co-Si and B-Si are respectively

\[ \Delta H_{\text{mix}}^{\text{Co-B}} = -24 \text{ kJ/mol, } \Delta H_{\text{mix}}^{\text{Co-Si}} = -38 \text{ kJ/mol, } \Delta H_{\text{mix}}^{\text{B-Si}} = -14 \text{ kJ/mol} \]  

[7], which favor Co-B and Co-Si clustering. We take the intersection point Co_{68.6}B_{25.2}Si_{5.7} of primary Co_{8}B_{3}-Si cluster line and subsidiary Si-centered cuboctahedron Co_{12}Si-B (Δ_{Co12Si} = 17.1 %, R_{Si}=0.132 nm) cluster line as the basic composition (figure 7), which cannot form BMG. Then, 4 at. % Nb is added to alloy the basic composition, and the quaternary composition (Co_{8}B_{3}-Si)_{0.9}Nb_{0.1} (Co_{68.6}B_{25.2}Si_{5.7}Nb_{4}) is the optimum BMG composition. This composition can also be interpreted with the cluster-plus-glue-atom model (cluster)(glue atom): (Co_{8}B_{3})_{1}M_{1}=TM_{68.7}B_{25}M_{8.3}, where glue atom M=(Si, Nb) linking TM_{8}B_{3}. This formula agrees with the
experimental composition \((\text{Co}_{0.68}\text{B}_{25.7}\text{Si}_{5.7})_{0.8}\text{Nb}_{0.4}\) = \(\text{Co}_{0.65}\text{B}_{24.7}\text{Si}_{5.6}\text{Nb}_{0.4}\) = \(\text{Co}_{0.8}\text{B}_{3}\text{Si}_{0.66}\text{Nb}_{0.48}\) = \(\text{Co}_{0.8}\text{B}_{3}\text{M}_{1.14}\).

Figure 7. Schematic composition chart of Co-B-Si ternary system.

So is the Fe-B-Y-Nb quaternary system [28]. The optimum BMG composition is the one developed by 3 at. % Nb minor-alloying of the basic composition \(\text{Fe}_{0.68}\text{B}_{25.7}\text{Y}_{3.7}\) which is the intersection of dense-packed Archimedean antiprism \(\text{Fe}_{8}\text{B}_{3}\text{Y}\) cluster line and Fe-centered icosahedral \(\text{Fe}_{12}\text{Y-B}\) cluster line \((\Delta \text{Fe}_{12}\text{Y} = 7.1\% , R = 0.180\ nm)\). This composition \(\text{Fe}_{0.68}\text{B}_{25.7}\text{Y}_{3.7}\) agrees perfectly with \(\text{Fe}_{4}\text{B}_{3}\text{Y}\text{M}_{1}\) (M=Y, Nb) model: \(\text{Fe}_{8}\text{B}_{3}\text{Y}_{0.66}\text{Nb}_{0.36}\) = \(\text{Fe}_{8}\text{B}_{3}\text{Y}_{0.66}\text{Nb}_{0.36}\) = \(\text{Fe}_{8}\text{B}_{3}\text{Y}_{0.66}\text{Nb}_{0.36}\).

From the above analysis, we see that the optimum BMG compositions are closely related with the primary cluster lines defined with dense-packed clusters. The subsidiary cluster lines determine the glue atom environment to connect the primary clusters. The maximum number of glue atoms is 3, which coincides with the fact that besides octahedral interstices, glue atoms takes all the tetrahedral interstices in an \(\text{fcc}\)-like structure according to the efficient-cluster-packing model [23]. An \(\text{fcc}\) unitcell includes four lattice sites, four octahedral interstices and eight tetrahedral interstices. Thus the ratio of the number of atoms to that of octahedral and tetrahedral interstices is 1:3. The ratio 1:1 for the number of clusters to that of glue atoms indicates that glue atoms only occupy the octahedral interstices, while the ratio 1:3 indicates the glue atoms takes all the octahedral and tetrahedral interstices.

3.6. Predictions of BMG compositions
Based on the cluster-plus-glue-atom model of \((\text{cluster})_1(\text{glue atom})_1\), new series of ternary TM-based alloy compositions \(\text{TM}_n\text{B}_3\text{M}_1\), \(\text{TM} = \text{Fe}, \text{Co}, \text{Ni}; \text{M} = \text{Nb}, \text{Ag}, \text{Si}, \text{Y}, \text{Ta}, \text{Mo}, \text{Ti}\) can be designed. Since the Archimedean antiprism \(\text{Ni}_3\text{B}_3\) is efficiently dense-packed with \(\Delta = 2.5\%\), we have designed and obtained \(\text{Fe}_8\text{B}_3\text{Y}_{0.66}\text{Nb}_{0.36}\) and \(\text{Ni}_3\text{B}_3\text{Si}\) BMG bars with a diameter of 2 mm, indicating the validity of the cluster-plus-glue-atom model in predicting good BMG compositions.
4. Conclusions
The cluster line approach has deciphered successfully the composition characteristics in different ternary quasicrystal- and bulk metallic glass-forming systems. A ternary quasicrystal and bulk metallic glass composition is located at the intersection point of two cluster lines, one generally being a dense-packed cluster line. The other cluster line plays a subsidiary role to determine the number of glue atoms. All these compositions are related with dense-packed clusters plus glue atoms, and can thus be expressed by a cluster-plus-glue-atom model. This model can be used to predict new ternary bulk metallic glasses as exemplified by (Fe₈B₃)₁Nb₁ and (Ni₈B₃)₁Si₁. The dense-packed clusters are CN₁₂ icosahedrons, CN₁₀ capped Archimedean antiprisms and CN₉/CN₁₁ capped trigonal prisms.

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References
[1] Steurer W 2004 Z. Kristallogr. 219 391
[2] Häussler P and Barzola-Quiqueta J 2002 J. Non-Cryst. Solids 312-314 498
[3] Dong C, Wang Q, Qiang J B, Wang Y M, Jiang N, Han G, Li Y H, Wu J and Xia J H 2007 J. Phy. D: Appl. Phys. 40 R1
[4] Dong C, Qiang J B, Wang Y M, Jiang N, Wu J and Thiel P 2006 Philo. Mag. 86 263
[5] Xia J H, Qiang J B, Wang Y M, Wang Q and Dong C 2006 Appl. Phys. Lett. 88 101907
[6] Wang Q, Dong C, Qiang J B and Wang Y M 2007 Mater. Sci. & Eng. A 449-451 18
[7] Boer de F R and Pettifor D G 1989 Cohesion in metals and transition metal alloys (Amsterdam: North Holland) p 167
[8] Demange V and Dubois J M 2004 Crystallography Rev. 10 111
[9] Ranganathan S, Chattopadhyay K, Singh A and Kelton K F 1997 Prog. Mater. Sci. 41 195
[10] Tsai A P 2003 Acc. Chem. Res. 36 31
[11] Miracle D B and Sanders W S 2003 Philos. Mag. 83 2409
[12] Barbier J N, Tamura N and Verger-Gaugry J L 1993 J. Non-Cryst. Solids 153-154 126
[13] Molokanov V V and Chebotnikov V N 1990 J. Non-Cryst. Solids 117-118 789
[14] Kelton K F, Kim W J and Stroud R M 1997 Appl. Phys. Lett. 70 3230
[15] Qiang J B, Wang Y M, Wang D H, Kramer M and Dong C 2003 Philo. Mag. Lett. 83 467
[16] Inoue A, Shen B L and Takeuchi A 2006 Mater. Trans. JIM 47 1275
[17] Köster U, Meinhardt J, Roos S and Liebertz H 1996 Appl. Phys. Lett. 69 179
[18] Saida J, Matsushita M and Inoue A 2001 Appl. Phys. Lett. 79 412
[19] Yang L, Xia J H, Wang Q, Dong C, Chen L Y, Ou X, Liu J F, Jiang J Z, Klementiev K, Saksl K, Franz H, Schneider J R and Gerward L 2006 Appl. Phys. Lett. 88 241913
[20] Wang Y M, Shek C H, Qiang J B, Wong C H, Wang Q, Zhang X F and Dong C 2004 Mater. Trans. JIM 45 1180
[21] Wang Y M, Shek C H, Qiang J B, Dong C, Pang S J and Zhang T 2007 J. Alloys Comp. 434-435 167
[22] Wu J, Wang Q, Qiang J B, Wang Y M and Dong C 2007 J. Mater. Res. 22 573
[23] Miracle D B 2006 Acta Mater. 54 4317
[24] Wang D, Tan H and Li Y 2005 Acta Mater. 53 2969
[25] Lu Z P and Liu C T 2004 J. Mater. Sci. 39 3965
[26] Inoue A, Zhang T and Masumoto T 1990 Mater. Trans. JIM 31 177
[27] Wang Y M, Qiang J B, Wong C H, Shek C H and Dong C 2003 J. Mater. Res. 18 642
[28] Wang Q, Cheng X, Zhun C L, Chen W R, Li Y H, Wu J, Qiang J B, Wang Y M and Dong C 2007 submitted to Acta mater.