SCIENTIFIC REPORTS

Received: 10 May 2015 Accepted: 03 September 2015 Published: 14 December 2015

OPEN Composition formulas of binary eutectics

Y. P. Ma^{1,2}, D. D. Dong¹, C. Dong¹, L. J. Luo¹, Q. Wang¹, J. B. Qiang¹ & Y. M. Wang¹

The present paper addresses the long-standing composition puzzle of eutectic points by introducing a new structural tool for the description of short-range-order structural unit, the cluster-plus-glueatom model. In this model, any structure is dissociated into a 1st-neighbor cluster and a few glue atoms between the clusters, expressed by a cluster formula [cluster] glue. This model is applied here to establish the structural model for eutectic liquids, assuming that a eutectic liquid consist of two subunits issued from the relevant eutectic phases, each being expressed by the cluster formula for ideal metallic glasses, i.e., [cluster](glue atom)1 or 3. A structural unit is then composed of two clusters from the relevant eutectic phases plus 2, 4, or 6 glue atoms. Such a dual cluster formulism is well validated in all boron-containing (except those located by the extreme phase diagram ends) and in some commonly-encountered binary eutectics, within accuracies below 1 at.%. The dual cluster formulas vary extensively and are rarely identical even for eutectics of close compositions. They are generally formed with two distinctly different cluster types, with special cluster matching rules such as cuboctahedron plus capped trigonal prism and rhombidodecahedron plus octahedral antiprism.

In a typical eutectic reaction, two solid phases transform to or from a single liquid phase at a specific composition and temperature. In spite of the obvious fundamental as well as engineering interests in such alloys, important especially for their low-melting points, the structures and compositions of eutectic liquids remain open issues. It is widely accepted that a eutectic liquid is characterized by topologic and chemical short-range-order clusters that maintain certain similarities with the eutectic phase structures¹⁻⁹. These alloys in liquid state at temperatures not far from the melting point were considered as cluster solutions, where these clusters are self-associated atomic groups or chemically ordered structural units¹. According to first-principles molecular dynamics simulations for liquid and undercooled eutectic alloys Au-(Si,Ge) at various temperatures², the local structure presents a well-defined chemical short-range order that enhances dissimilar element interactions in contrast with random solid mixture and may explain the high stability of the liquid phase on the basis of preferential Au-(Si,Ge) bonds. However, the available information on the short-range-order structures in eutectic melts is far from complete and the structures and composition rules of eutectics are largely unknown.

Necessarily a short-range-order structural model is required for any understanding about the structures and compositions of the eutectic points. Actually binary eutectic compositions frequently occur near simple composition ratios¹⁰ such as 8/1, 5/1, 3/1, 2/1 and 3/2. Based on Frank's conjecture¹¹ that icosahedral cluster might be responsible for liquid undercooling, these ratios were tentatively explained as chained arrangements of icosahedral clusters with the lowest solute atom neighbors¹². These simple ratios were recently addressed¹³ using the dense cluster-packing model for metallic glasses¹⁴. The eutectic liquid was treated as being composed of efficiently packed solute-centered atomic clusters where are present four topologically distinct atomic sites. Choosing different coordinate close-packing clusters and changing the occupation style of the interstitial solutes, simple ratios of binary eutectics could be reached. A similar model for metallic glasses was also proposed¹⁵ where shared quasi-equivalent clusters are packed into an icosahedral-like structure, which explained some binary eutectics and metallic compositions near the solid solution side of binary phase diagrams. However, all these efforts fail in interpreting quantitatively the occurrence of eutectics at various and specific compositions. For this objective, a structural model, enabling a quantitative description of short-range orders, is required to describe precisely the eutectic liquid structure. It is reasonable to anticipate that a structural unit, reflecting the characteristic short-range ordering in the liquid, should be present for a specific eutectic composition.

¹Key Laboratory of Materials Modification (Ministry of Education), School of Materials Science & Engineering, Dalian University of Technology, Dalian 116024, China. ²Special Glass Key Laboratory of Hainan Province, School of Materials and Chemical Engineering, Hainan University, Haikou 570228. Correspondence and requests for materials should be addressed to C.D. (email: dong@dlut.edu.cn)

We have developed a so-called cluster-plus-glue-atom model that suits specifically for short-range-order structure descriptions in quasicrystals, amorphous alloys¹⁶, and solid solutions¹⁷. In this model, any structure is dissociated into a 1st-neighbor coordination polyhedral cluster and a glue-atom part that are situated outside the cluster part at the 2nd neighbors and beyond. Then the structure can be expressed by a cluster formula [cluster]glue_{xx} where the cluster is the coordination polyhedron representative of the 1st-neighbor short-range order of the structure (notice that the term cluster may mean any agglomeration of atoms in a general sense, but here we confine the cluster concept to cover only the 1st-neighbor coordination polyhedra), and the glue atoms between the clusters mark the short-range-order feature on and beyond the 2nd neighbors. For a bulk metallic glass, the number of glue atoms is either 1 or 3^{16,18}. It was further pointed out^{19,20} that the total number of valence electrons per unit cluster formula for an ideal bulk metallic glass is universally about 24, so that the cluster formula for a bulk metallic glass resembles the 'molecular' unit of a chemical substance²⁰. This formula can also be understood as arising from a certain spatial averaging scheme of a complicated disordered structure into a short-range-order structural unit of a dozen of atoms, covering only the first few neighbors, generally 1st and 2nd. It should be emphasized that the clusters are assumed to be isolated from each others in metallic glasses, which is necessary to avoid the center-shell type of nearest-neighbor short-range orders to develop into longer-range ones. Solid-solution alloys have been treated in a similar manner, because they are also characterized by chemical short-range orders, and the formulas well explain the industrial specification composition selection, as exemplified by Cu-Zn and Cu-Ni allovs¹⁷.

In the following, the cluster-plus-glue-atom structural model and the relevant composition formulas for eutectic liquids will first be proposed, and then boron-containing binary eutectics will be fully covered using this model. It will be shown that, at least for normal eutectics whose compositions do not fall too close to the phase diagram terminals, the model applies perfectly, which arrives at formulated eutectic compositions within accuracies below 1 at.% from experimental ones.

Cluster-plus-glue-atom model for binary eutectic liquids

A binary eutectic alloy liquid normally decomposes in a coupled growth mode into two eutectic phases with distinct composition differences. It is then reasonable to assume that the eutectic liquid would contain two subunits that evolve towards their respective eutectic phases. Thereof we propose the first assumption for modeling the eutectic liquids:

1) A eutectic liquid is comprised of two subunits issued from the two eutectic phases.

As already stated, the compositions at which metallic glass stability reaches the maximum are well expressed by cluster formulas out of eutectic/devitrification phases in accordance with the cluster-plus-glue-atom model¹⁸. Since metallic glasses can be regarded as frozen liquids, their formulas in fact describe some stable liquids that resist crystallization upon solidification. Also metallic glass formation is generally associated with eutectics. Thereof we introduce the second assumption:

2) Each subunit is described by a cluster formula of ideal metallic glasses, expressed as [cluster](glue atoms)_{1 or 3}

A eutectic liquid is then composed of two subunit liquids, each being formulated either by [cluster](glue atoms)₁ or by [cluster](glue atoms)₃, so that the final eutectic composition is expressed by a dual cluster formula:

$$[cluster_{\alpha} + cluster_{\beta}](glue atoms)_{2 \text{ or } 4 \text{ or } 6}$$
(1)

where the two clusters in the brackets belong respectively to the two liquid subunits and are inherited from corresponding eutectic phases α and β .

The eutectic composition interpretation then relies on the identification of the right clusters from the eutectic phases. In explaining a bulk metallic glass composition, the cluster is taken from a known crystalline phase, assuming local structural heritage between the two states. In a given crystal structure, however, there are often multiple nearest-neighbor clusters (centered by any non-equivalent site in unit cell is defined a cluster). Among the multiple clusters, there must be at least one cluster, termed 'the principal cluster'²¹, that represents the dominating short-range order feature of the structure. This principal cluster should be the most strongly bonded part in the structure, which leads to high cluster isolation and atomic dense packing, as well as high elastic coefficients²². The atomic dense packing of a cluster could be measured by the center-to-shell atomic radius ratios, because an ideally densely-packed cluster of certain coordination number (CN) shows a special such ratio¹⁴. Cluster isolation refers to the cluster size reduction to account for the commonly present cluster overlapping in crystals, and the principal one should show the highest cluster separation.

For instance, the BCo₃ phase (CFe₃ structure type, space group Pnma, the crystal structure data are all from Pearson's handbook²³) contains sixteen atoms in its unit cell, which belong to three non-equivalent sites: four B at (0.881, 0.25, 0.431), four Co at (0.044, 0.25, 0.837), and eight Co (0.181, 0.063, 0.337). Centered by these sites are



and CN14 [Co-B₃Co₁₁]

(Fig. 1). In expressing a cluster, the central atom is placed first and is

separated from the nearest-neighbor shell atoms by a hyphen. Their atomic radius ratios of the central atom over that of the shell atoms are respectively 0.70, 1.07, and 1.07, calculated from the B covalent radius of 0.088nm and the Co Goldschmidt radius of 0.125 nm. All being quite close to those of the ideally dense-packed clusters of CN9



Figure 1. Clusters in BCo₃ (the CFe₃ structure). Small spheres represent B and large ones Co. Projection along [001].

(0.71), CN15 (1.12) and CN14 (1.05), the dense packing property alone cannot distinguish effectively the clusters. These clusters are all extensively overlapped with neighboring ones, and the reduced clusters become respectively [B-Co₃], [Co-B₁Co₂], and [Co-B_{0.5}Co_{0.5}], which are also phase formulas expressed using the three clusters because there is no glue atoms. The cluster reduction rates are respectively 4/9, 3/16, and 1.5/15. Therefore the principal cluster should be CN9 [B-Co₉] for the highest cluster isolation. This cluster type is frequently encountered in explaining eutectic points.

In the above example, the phase structure is completely occupied by the clusters and the phase formulas expressed using the clusters do not contain the glue atom part. In many cases, such as in B_4 Y, glue atoms are involved. There are four non-equivalent sites in the unit cell of B_4 Y (B_4 Th structure type, space group P4/mbm), four B at (0, 0, 0.2027), four Y at (0.3179, 0.8179, 0), four B at (0.0871, 0.5871, 0.5), and eight B at (0.1757, 0.0389,

0.5). Four clusters are then defined centered by each of the four non-equivalent sites, i.e., [B-B₃]



 $[Y-B_{18}Y_5]$ gives a satisfactory atomic radius ratio of 1.67, calculated from the central atom B radius of 0.088 nm and the averaged atomic radius $B_{18}Y_5$ of 0.108 nm (0.18 nm for Y), which compares favorably with the ideal value of 1.61 for the CN23 cluster. The reduced clusters after overlapping are respectively [B-B], [B-B_2], [B-B_3], and [Y-B_4]. In terms of the absolute size, the last one is the largest but in comparison with the complete cluster size, it is not. Such a contradiction actually originates from the fact that glue atoms are involved: the phase formulas expressed by the four clusters are respectively [B-B]B_2Y, [B-B_2]BY, [B-B_3]Y, and [Y-B_4]. Since the principal cluster should dominate the phase structure, the smallest number of glue atoms are desirable, so that the last one [Y-B_{18}Y_5] is finally selected.

In many cases, the principal clusters can be directly identified from the phase formulas, where the largest phase formula, the smallest cluster size reduction, and the smallest number of glue atoms serve the finger prints for the principal clusters. A phase formula can simply be arrived at by matching the atomic multiplicity of each atom in unit cell. For instance, to reach the phase formula expressed by the $[B-Co_9]$ cluster, the multiplicity of the central B atom being 4, and those of the two Co non-equivalent sites bring 4 and 8, the reduced cluster becomes $[B_1-Co_1Co_2] = [B-Co_3]$, which is also the phase formula for the absence of glue atoms here. The use of atomic dense packing is restricted, for atoms are not strictly spherical of constant atomic radii. In the following, the phase formula characteristics are mainly used to determine the principal cluster.

After choosing the principal clusters from two eutectic phases, according to formula (1), one pair of such clusters are matched with two, four, and six glue atoms, giving a dual cluster formula for the eutectic liquid. In the following, B-Co eutectics are explored in detail to exemplify the composition interpretation procedures using the principal clusters from respective eutectic phases.

The B-Co system contains three eutectic points, exemplifying three major types, metal-compound, compound-compound, and compound-boron (Fig. 2). In the present paper, the phase diagrams are all readapted from ref. 24.

The eutectic $B_{18.5}Co_{81.5}$ involves eutectic phases α -Co and BCo₃. α -Co has the Mg structure, which presents a unique twinned cuboctahedron CN12 cluster, typical for the hexagonal close-packed metals. This CN12 [Co-Co₁₂] cluster together with CN9 [B-Co₉] from BCo₃, plus four B glue atoms, explain the experimental eutectic as

two



Figure 2. Interpretation of B-Co eutectic points. The dual-cluster formulas come from eutectic phases α -Co-BCo₃, BCo₂-BCo, and BCo- β -B.

 $\begin{array}{l} B_{18.5} Co_{81.5} \rightarrow [Co-Co_{12}+B-Co_{9}] B_{4} = B_{5} Co_{22} \approx B_{18.5} Co_{81.5}, \mbox{ where the clusters come from Co (Mg) and BCo_{3} (CFe_{3}), \mbox{ as shown in Fig. 2 (the cluster configurations are also marked) and Table 1. \end{array}$

The eutectic B₃₇Co₆₃ involves eutectic phases BCo₂ and BCo. BCo₂ is of the AlCu₂ type and presents two clusters,

B-centered octahedral antiprism CN10 [B-B₂Co₈]



and Co-centered CN15 [Co-B₃Co₁₂]



The phase formulas expressed by the two clusters are $[B-Co_2]$ and $[Co-B_{0.5}]$, respectively. The

principal cluster is then the former cluster $[B-B_2Co_8]$ that produces a larger phase formula. This is also a common cluster type in eutectic formulas.

BCo is of the BFe structure and presents two types of clusters, capped trigonal prism CN9 [B-B₂Co₇]



with two of the three capping Co atoms replaced by B atoms. The phase formulas expressed by the two clusters are respectively [B-Co] and [Co-B], both containing two atoms. Both are taken as the principal clusters. The eutectic $B_{37}Co_{63}$ is explained using both clusters, as shown in Fig. 2 and Table 1:

 $B_{37}Co_{63} \rightarrow [B - B_2Co_8 + B - B_2Co_7]B_4Co_2 = [B - B_2Co_8 + Co - B_7Co_6]Co_2 = B_{10}Co_{17} \approx B_{37.0}Co_{63.0}, \label{eq:basic}$ where the clusters come from BCo_2 (Al_2Cu) and BCo (BFe).

The eutectic $B_{61}Co_{39}$ involves BCo and β -B. Although the boron structures are generally analyzed as based on B_{12} icosahedron, the unique local structure in terms of the nearest-neighbor coordination polyhedron is, however,

the pentagonal pyramid [B-B₆]

, and the commonly-used B_{12} icosahedron is actually formed by twelve

such pyramids enclosing an empty center.

The B-richest eutectic is explained as

 $B_{61}Co_{39} \rightarrow [B - B_2Co_7 + B - B_6]B_4Co_2 = [Co - B_7Co_6 + B - B_6]Co_2 = B_{14}Co_9 \approx B_{60.9}Co_{39.1}$, where the clusters come from BCo (BFe) and β -B, as shown in Fig. 2 and Table 1. Again the two principal clusters from BCo are both used.

The deviations between the calculated and experimental compositions are respectively $(100*5/22-18.5)*\sqrt{2} \approx 0.0$ (a scale of $\sqrt{2}$ should be used to reach the real composition distance), $(100*10/27-37.0)*\sqrt{2} \approx 0$, $(100*14/23-61)*\sqrt{2} \approx -0.1$ at.% B (the negative sign means that the calculated composition is slightly B leaner than the experimental one), which are well below the normal experimental accuracy of about 1 at. %. The deviations are listed in Table 1 and are not mentioned below because they all lie within 1 at.% accuracy.

In reaching the final eutectic formulas using the two principal clusters from relevant eutectic phases, different combinations of glue atoms have been attempted and in general there is only one solution that fits the experimental eutectic point. For instance, the principal clusters $[Co-Co_{12}]$ from eutectic phase Co and $[B-Co_9]$ from eutectic phase BCo₃, in combination with different glue atoms $(B,Co)_{2,4,6}$, produce dual cluster formulas $[Co-Co_{12} + B-Co_9]$ (B,Co)_{2,4,6}, with their total number of atoms per unit formula being 25, 27, and 29. These numbers times the

Exp. eutectics	Cal. Eutectics (deviation in at.% B)	Eutectic phases (structural types)	Dual cluster formulas and near-integer ratios
B _{11.4} Be _{88.6}	B _{11.1} Be _{88.9} (-0.4)	$BBe_4 (BBe_4) + \alpha - Be (Mg)$	$[B-Be_9+Be-Be_{12}]B_2Be_2=B_3Be_{24}=BBe_8$
B17Sc83	B _{17.2} Sc _{83.8} (0.3)	α -Sc (Mg) + B ₂ Sc (AlB ₂)	$[Sc-Sc_{12}+B-B_{3}Sc_{6}]BSc_{5}=B_{5}Sc_{24}=BSc_{4.8}$
B ₈₃ Sc ₁₇	B _{82.6} Sc _{17.4} (−0.6)	$B_2Sc (AlB_2) + B_{12}Sc (B_{12}U)$	$[Sc-B_{12}Sc_6 + Sc-B_{24}]B_2 = B_{38}Sc_8 \approx B_{4.7}Sc$
	$B_{83,3}Sc_{16,7}(0.5)$		$[Sc-B_{12}Sc_6 + Sc-B_{24}]B_4 = B_{40}Sc_8 = B_5Sc$
B ₉₄ Sc ₆	$B_{94.1}Sc_{5.9}(0.2)$	$B_{12}Sc (B_{12}U) + \beta - B$	$[Sc-B_{24}+B-B_6](BSc) = B_{32}Sc_2 = B_{16}Sc$
B _{25.5} Y _{74.5}	B _{25.9} Y _{74.1} (0.6)	α -Y (Mg) + B ₂ Y (AlB ₂)	$[Y-Y_{12} + B-B_3Y_6]B_3Y = B_7Y_{20} \approx BY_{2.9}$
B70Y30	B _{69.4} Y _{30.6} (-0.9)	$B_2Y (AlB_2) + B_4Y (B_4Th)$	$[Y \! - \! B_{12}Y_6 \! + Y \! - \! B_{18}Y_5]B_4Y_2 \! = \! B_{34}Y_{15} \! \approx B_4Y_{9.1}$
$B_{96}Y_{4}$	B _{96.4} Y _{3.6} (0.6)	$B_{12}Y (B_{12}U) + B_{66}Y (B_{66}Y)$	$[Y \! - \! B_{24} + Y_{0.5} \! - \! B_{14.56}]B_2 \! = \! B_{40.56}Y_{1.5} \! \approx B_{27.0}Y$
$B_{14}Zr_{86}$	$B_{13.8}Zr_{86.2}(-0.3)$	$B_2Zr (AlB_2) + \beta - Zr (W)$	$[B\!-\!B_3\!Zr_6\!+\!Zr\!-\!Zr_{14}]Zr_4\!=\!B_4\!Zr_{25}\!\approx BZr_{6.2}$
B13Hf87	$B_{12.5}Zr_{87.5}(-0.7)$	BHf (ClNa) + β -Hf (W)	$[\mathrm{B}\mathrm{-}\mathrm{H}\mathrm{f}_6\mathrm{+}\mathrm{H}\mathrm{f}\mathrm{-}\mathrm{H}\mathrm{f}_{14}]\mathrm{B}_2\mathrm{=}\mathrm{B}_3\mathrm{H}\mathrm{f}_{21}\mathrm{=}\mathrm{B}\mathrm{H}\mathrm{f}_7$
$B_{15}V_{85}$	B _{14.7} V _{85.3} (-0.4)	$V(W) + B_2 V_3 (Si_2 U_3)$	$[V - V_{14} + V - B_4 V_{10}] BV_3 = B_5 V_{29} \approx BV_{5.8}$
B ₁₄ Nb ₈₆	$B_{13.9}Nb_{86.1}(-0.2)$	$B_2Nb_3 (Si_2U_3) + Nb (W)$	$[Nb - B_4 Nb_{10} + Nb - Nb_{14}]BNb_5 = B_5 Nb_{31} \approx BNb_{6.2}$
B52Nb48	$B_{51.5}Nb_{48.5}(-0.7)$	$B_4Nb_3 (B_4Ta_3) + BNb (BCr)$	$[Nb - B_{12}Nb_6 + B - B_2Nb_7]Nb_2B_2 = B_{17}Nb_{16} \approx B_{1.1}Nb$
B ₂₃ Ta ₇₇	B _{23.3} Ta _{76.7} (0.5)	$BTa_2 (Al_2Cu) + Ta (W)$	$[B - B_2 T a_8 + T a - T a_{14}] B_4 = B_7 T a_{23} \approx B T a_{3.3} \approx B_3 T a_{10}$
B ₆₁ Ta ₃₉	B _{61.4} Ta _{38.6} (0.5)	$B_2Ta (AlB_2) + B_4Ta_3$	$[Ta - B_{12}Ta_6 + Ta - B_{12}Ta_6]Ta_3B_3 = B_{27}Ta_{17} \approx B_{3.2}Ta_2$
B _{13.5} Cr _{86.5}	$B_{13.3}Cr_{86.7}(-0.2)$	$Cr(W) + BCr_2(Al_2Cu)$	$[Cr-Cr_{14}+B-B_2Cr_8]BCr_3=B_4Cr_{26}=B_2Cr_{13}$
B _{53.5} Cr _{46.5}	$B_{53.5}Cr_{46.5}(-0.0)$	$BCr + B_4Cr_3 (B_4Ta_3)$	$[Cr\!-\!B_7Cr_{10}\!+\!Cr\!-\!B_{12}Cr_6]B_4Cr_2\!=\!B_{23}Cr_{20}\!\approx B_{1.1}Cr$
B23Mo77	B _{23.3} Mo _{76.7} (0.5)	$Mo(W) + BMo_2(Al_2Cu)$	$[Mo-Mo_{14}+B-B_2Mo_8]B_4 = B_7Mo_{23} \approx BMo_{3.3} \approx B_3Mo_{10}$
$B_{27}W_{73}$	B _{26.7} W _{73.3} (-0.5)	$W(W) + BW_2(Al_2Cu)$	$[B\text{-}W_{14} + B\text{-}B_2W_8]B_4 = B_8W_{22} \approx B_3W_8$
B43W57	B _{42.9} W _{57.1} (-0.2)	$BW_2 (Al_2Cu) + \beta - BW (BCr)$	$\begin{split} & [B\text{-}B_2W_8 + B\text{-}B_3W_7]B_5W = B_{12}W_{16} = B_3W_4 \\ & [B\text{-}B_2W_8 + W\text{-}B_7W_{10}]B_5W = B_{15}W_{20} = B_3W_4 \end{split}$
B ₆₃ W ₃₇	$B_{63.0}W_{37.0}(0.0) B_{63.2}W_{36.8}(0.2)$	$\beta\text{-BW}(BCr) + B_5W_2(B_5Mo_2)$	$\begin{split} & [B\text{-}B_3W_7 + W\text{-}B_{13}]W_2 \!=\! B_{17}W_{10} \!\approx B_{5,1}W_3 \\ & [W\text{-}B_7W_{10} \!+ W\text{-}B_{13}]B_4W_2 \!=\! B_{24}W_{14} \!\approx B_{5,1}W_3 \end{split}$
B _{14.3} Mn _{85.7}	$B_{14.3}Mn_{85.7}(-0.0)$	δ-Mn (W) + BMn ₂ (Al ₂ Cu)	$[Mn - Mn_{14} + B - B_2Mn_8]BMn = B_4Mn_{24} = BMn_6$
B37Mn63	B _{37.0} Mn _{63.0} (0.0)	$BMn_2 (Al_2Cu) + BMn (BFe)$	
B _{61.5} Mn _{38.5}	$B_{61.4}Mn_{38.6}(-0.2)$	$B_4Mn_3 (B_4Ta_3) + BMn_2 (AlB_2)$	$ [Mn - B_{12}Mn_6 + Mn - B_{12}Mn_6]B_3Mn_3 = B_{27}Mn_{17} \approx \\ B_{3,2}Mn_2 $
$B_{17}Fe_{83}$	$B_{16.7}Fe_{83.3}(-0.5)$	γ -Fe (Cu) + BFe ₂ (Al ₂ Cu)	$[Fe - Fe_{12} + B - B_2 Fe_8]B_2 Fe_4 = B_5 Fe_{25} = BFe_5$
$B_{64}Fe_{36}$	B _{64.5} Fe _{35.5} (0.7)	BFe (BFe) $+\beta$ -B	$[Fe-B_7Fe_{10}+B-B_6]B_6=B_{20}Fe_{11}\approx B_{1.8}Fe$
B _{18.5} Co _{81.5}	B _{18.5} Co _{81.5} (0.0)	α -Co (Mg) + BCo ₃ (CFe ₃)	$[\text{Co-Co}_{12} + \text{B-Co}_9]\text{B}_4 = \text{B}_5\text{Co}_{22} \approx \text{B}_2\text{Co}_9$
B ₃₇ Co ₆₃	B _{37.0} Co _{63.0} (0.0)	$BCo_2 (Al_2Cu) + BCo (BFe)$	$ \begin{bmatrix} B - B_2 Co_8 + B - B_2 Co_7 \end{bmatrix} B_4 Co_2 = \begin{bmatrix} B - B_2 Co_8 + Co - B_7 Co_6 \end{bmatrix} \\ Co_2 = B_{10} Co_{17} = B_3 Co_{5,1} $
B ₆₁ Co ₃₉	B _{60.9} Co _{39.1} (-0.1)	BCo (BFe) + β -B	$ \begin{array}{c} [B - B_2 Co_7 + B - B_6] B_4 Co_2 = [Co - B_7 Co_6 + B - B_6] \\ Co_2 = B_{14} Co_9 \approx B_{3.1} Co_2 \end{array} $
B ₁₇ Ni ₈₃	B _{17.2} Ni _{82.8} (0.3)	Ni (Cu) + BNi ₃ (CFe ₃)	$[Ni - Ni_{12} + B - Ni_9]B_4Ni_2 = B_5Ni_{24} = B_5Ni_{4.8}$
B30Ni20	$B_{29.6}Ni_{70.4}(-0.5)$	$BNi_3 (CFe_3) + BNi_2 (Al_2Cu)$	$[B\text{-}Ni_9 + B\text{-}B_2Ni_8]B_4Ni_2 = B_8Ni_{19} \approx B_3Ni_{7.1}$
B _{39.5} N _{60.5}	$B_{39.4}Ni_{60.6}(-0.1)$	$BNi_2(Al_2Cu) + o-B_3Ni_4$	$\begin{array}{l} [B\text{-}B_2Ni_8 + Ni\text{-}B_6Ni_{11}]B_4 \!=\! [B\text{-}B_2Ni_8 \!+ Ni\text{-}B_7Ni_{10}] \\ B_3Ni \!=\! B_{13}Ni_{20} \!\approx\! B_2Ni_{3.1} \end{array}$
B45.3Ni54.7	B _{45.7} Ni _{54.3} (0.6)	m-B ₃ Ni ₄ + BNi (BCr)	$[B\text{-}B_2\text{Ni}_8 + \text{Ni}\text{-}B_7\text{Ni}_{10}]B_6 \!=\! B_{16}\text{Ni}_{19} \!\!\approx B\text{Ni}_{1.2}$
B _{24.2} Pd _{75.8}	B _{24.1} Pd _{77.8} (-0.1)	$Pd(Cu) + B_3Pd(CFe_3)$	$[Pd-Pd_{12}+B-Pd_9]B_6 = B_7Pd_{22} \approx BPd_{3.1}$
B _{34.6} Pd _{65.4}	B _{34.8} Pd _{65.2} (0.3)	$B_3Pd(CFe_3) + \beta - B$	$[B-Pd_9 + B-B_6]Pd_6 = B_8Pd_{15} \approx BPd_{1.9}$
B71C29	$B_{70.6}C_{29.4}(-0.6)$	$B_{13}C_2(B_{13}C_2) + C(graphite)$	$[B-CB_5+C-C_3]B_6=B_{12}C_5=B_{4.8}C_2$

Table 1. Eutectic compositions in boron-containing binary systems and their interpretations using dualcluster formulas from eutectic phases. The deviation between the calculated and the measured compositionsare also shown.

experimental eutectic composition result in $25^{*}(B_{18.5}Co_{81.5}) = B_{4.625}Co_{20.375}$, $27^{*}(B_{18.5}Co_{81.5}) = B_{4.995}Co_{22.005}$, and 29^{*} ($B_{18.5}Co_{81.5}) = B_{5.365}Co_{23.635}$. The second formula, being the closest to an integer form B_5Co_{22} , is adopted to explain the eutectic, $B_5Co_{22} \approx B_{18.5}Co_{81.5}$. The other two are too much deviated from any integer forms by about 2 at.% B.

In the next section, well-established boron-containing binary eutectics are analyzed in the same manner, and they are all well explained by dual-cluster eutectic formulas using the principal clusters derived from relevant eutectic phases.

Dual cluster formulas of boron-containing binary eutectics

The boron-containing systems are analyzed in the sequence of element groups in the periodic table.

1) IIA element Be

Among the B-IIA binary systems, only B-Be presents a eutectic-type phase diagram at $B_{11,4}Be_{88,6}$, bounded by eutectic phases α -Be and BBe₄, α -Be has the same Mg structure as α -Co, and its cluster type is the CN12 twinned cuboctahedron [Be-Be₁₂]. BBe₄ presents four clusters, [B-Be₉], [Be-B₄Be₆], [Be-BBe₁₂], and [Be-B₂Be₁₀].

The corresponding phase formulas are respectively $[B-Be_4]$, $[Be-BBe_2]Be$, $[Be-BBe_2]Be$, and $[Be-B_{0,5}B_1]$. The first cluster [B-Be₉] is chosen as the principal cluster because it generates the largest phase formula of five atoms, [B-Be₄], without glue atoms. The eutectic point is explained with

 $B_{11,4}Be_{88,6} \rightarrow [B-Be_9 + Be-Be_{12}]B_2Be_2 = B_3Be_{24} \approx B_{11,1}Be_{88,9}, \text{ where the clusters come from BBe_4 and } \alpha - Be (Mg),$ as shown in Fig. 3 and Table 1.

2) IIIA elements Sc and Y

 α -(Sc,Y) of the Mg structure presents the CN12 twinned octahedral cluster.

B₂Sc is of the AlB₂ structure and presents two clusters, [Sc-B₁₂Sc₆] and capped trigonal prism [B-B₃Sc₆]. The phase formulas expressed by the two clusters are [Sc-B₂] and [B-Sc_{0.5}]. In transforming from the initial cluster $[Sc-B_{12}Sc_6]$ of 21 atoms to the final phase formula $[Sc-B_2]$ of 3, the size reduction rate is 3/21 = 0.14, which is comparable to that from $[B-B_3Sc_6]$ to $[B-Sc_{0.5}]$ with a size reduction rate of 1.5/10 = 0.15, signifying that both can be the principal clusters. The eutectic $B_{17}Sc_{83}$ is explained by $[B-B_3Sc_6]$ from BSc₂ and $[Sc-Sc_{12}]$ from Sc (Mg), as shown in Fig. 4 and Table 1:

$$B_{17}Sc_{83} \rightarrow [Sc - Sc_{12} + B - B_3Sc_6]BSc_5 = B_5Sc_{24} \approx B_{17.2}Sc_{83.8}$$

The B-rich cluster $[Sc-B_{12}Sc_6]$, containing too much B, cannot explain this eutectic point.

The $B_{12}Sc$ phase is of the $B_{12}U$ structure and presents two clusters, $[B-B_5]$ (square pyramid) and $[Sc-B_{24}]$. The phase formulas are respectively $[B]Sc_{1/12}$ and $[Sc-B_{12}]$, so that the latter cluster is selected as the principal cluster for the largest phase formula without glue atoms.

The B-rich eutectic B₈₃Sc₁₇ is explained with this [Sc-B₂₄], together with [Sc-B₁₂Sc₆] (B-rich) from B₂Sc (Fig. 4 and Table 1), expressed by

 $B_{83}Sc_{17} \rightarrow [Sc-B_{12}Sc_6 + Sc-B_{24}]B_2 = B_{38}Sc_8 \approx B_{82.6}Sc_{17.4} \text{ or by } [Sc-B_{12}Sc_6 + Sc-B_{24}]B_4 = B_{40}Sc_8 \approx B_{83.3}Sc_{16.7} + Sc_{17.4}Sc_{10}Sc$ The B-richest eutectic $B_{94}Sc_6$ is explained with:

 $B_{94}Sc_6 \rightarrow [Sc-B_{24} + B-B_6]BSc = B_{32}Sc_2 \approx B_{94,1}Sc_{5,9}$, where the clusters come from $B_{12}Sc$ ($B_{12}U$) and β -B (Fig. 4) and Table 1).

New structures encountered in the B-Y system are B₄Y and B₆₆Y.

The determination of principal cluster $[Y-B_{18}Y_5]$ in B_4Y (B_4 Th structure) has already been discussed earlier.

The B₆₆Y phase contains 1936 atoms in its unit cell, and the cluster centered by Y is taken as the principal cluster because it generates a phase formula of the largest size. Geometrically this cluster is expressed as [Y-YB₂₄]. However, due to the complicated site occupancies, the real coordination environment is $[Y_{0.5} - B^{13}_{4^{+}0.28}Y_{0.5}B^{6}_{2^{+}1}B^{5}_{2^{+}1}B^{12}_{4^{+}0.65}]$ $B^{10}_{4^*1}B^{11}_{4^*0.71} = [Y_{0.5}-B_{14.56}]$, where the superscripts indicate the atomic sites as in Pearson's handbook. This cluster configuration is not shown for its complexity in Fig. 5, where all the B-Y eutectics are explained (also in Table 1).

Like in B-Sc, the Y-richest eutectic $B_{25,5}Y_{74,5}$ is explained with $[Y-Y_{12}]$ from α -Y (Mg) and the Y-rich $[B-B_3Y_6]$ cluster from B₂Y (AlB₂):

$$B_{25,5}Y_{74,5} \rightarrow [Y - Y_{12} + B - B_3Y_6]B_3Y = B_7Y_{20} \approx B_{25,9}Y_{74,1}$$

Though the clusters are of the same types as the B-Sc case, the glue atoms are different. Actually, as will be further shown, eutectics are rarely the same, even for those of the nearly same chemistries and cluster structures.

The eutectic B70Y30 is explained with:

 $B_{70}Y_{30} \rightarrow [Y-B_{12}Y_6 + Y-B_{18}Y_5]B_4Y_2 = B_{34}Y_{15} \approx B_{69.4}Y_{30.6}$, where the two clusters are from the eutectic phases B_2Y (the B-rich cluster is used) and B_4Y .

The B₉₆Y₄ eutectic is explained with [Y-B₂₄] from B₁₂Y and [Y_{0.5}-B_{14.56}] from B₉₉Y: B₉₆Y₄ \rightarrow [Y - B₂₄ + Y_{0.5} - B_{14.56}]B₂ = B_{40.56}Y_{1.5} \approx B_{96.4}Y_{3.6}. The B-richest eutectic B₉₉Y₁, being located very close to the B end, is not explained.

Again it is noticed that eutectic formulas are rarely identical, despite very similar outer-electron configurations and cluster types in both systems. It is also worth pointing out that the eutectic formation generally involves certain cluster matching rules for the two types of clusters of different geometries and chemistries, which constitutes another general property of eutectic formulas.

3) IVA elements Zr and Hf

These systems are characterized by the presence of two terminal eutectics close to the two elemental ends. The B-Ti and all the B-rich eutectics, too close to phase diagram terminals, cannot be explained by any dual cluster formulas. The $B_{14}Zr_{86}$ and $B_{13}Hf_{87}$ eutectic points will be dealt with here. The former one is bounded by BCC β -Zr (W) and B₂Zr (AlB₂). The β -Zr structure presents a unique CN14 rhombi dodecahedral cluster [W-W₁₄], typical for BCC and its superstructures. This cluster, together with the Zr-rich [B-B₃Zr₆] cluster from B₂Zr (AlB₂), explain the experimental eutectic

 $B_{14}Zr_{86} \rightarrow [B-B_3Zr_6 + Zr-Zr_{14}]Zr_4 = B_4Zr_{25} \approx B_{13.8}Zr_{86.2}$ (Fig. 6 and Table 1).

The $B_{13}Hf_{87}$ eutectic is bounded by β -Hf (W) and BHf (ClNa), the latter being characterized by two octahedral clusters [B-Hf₆] and [Hf-B₆]. Both clusters, giving phase formulas of the same size of two atoms, but the former one is more densely packed (B being a small atom in the octahedral interstice site of Hf) and is taken as the principal cluster:

 $B_{13}Hf_{87} \rightarrow [B-Hf_6 + Hf-Hf_{14}]B_2 = B_3Hf_{21} = B_{12.5}Hf_{87.5}$ (Fig. 7 and Table 1).

Notice that, again, despite of the extreme similarities between Zr and Hf, even when their eutectics are quite near each other, they corresponds to different eutectic phases and henceforth different dual cluster formulas. 4) VA elements V, Nb, and Ta

These VA elements, like the IV ones, generally form terminal eutectics, except Ta that also forms an intermediate

eutectic in the middle part of the phase diagram. New structure types involved are $B_2(V,Nb)_3$, B(V,Nb), and B_4Nb_3 . $B_2(V,Nb)_3$ is of the Si₂U₃ structural type and presents rhombi dodecahedron [(V,Nb)-B₄(V,Nb)₁₀], capped trigo-

nal prism $[B-B(V,Nb)_8]$, and $[(V,Nb)-B_6(V,Nb)_{11}]$. The phase formulas expressed by these clusters are respectively



Figure 3. Interpretation of the B-Be eutectic point. The dual cluster formula comes from eutectic phases BBe_4 and α -Be.





 $[(V,Nb)-B_2(V,Nb)_2]$, $[B-(V,Nb)_{1,5}]$, and $[(V,Nb)-B_{0,5}(V,Nb)]$. The first cluster $[B-B(V,Nb)_8]$ should be the principal one for its largest phase formula size of five atoms.

The $B_4(Nb,Ta)_3$ phases are of the B_4Ta_3 structure and presents four clusters, two capped trigonal prisms $[B-B_2(Nb,Ta)_7]$ and $[B-B_3(Nb,Ta)_6]$, $[(Nb,Ta)-B_7(Nb,Ta)_8]$, and $[(Nb,Ta)-B_{12}(Nb,Ta)_6]$. The phase formulas are respectively two $[B-B(Nb,Ta)_{1,5}]$, $[(Nb,Ta)-B_2(Nb,Ta)_{0,5}]$, and $[(Nb,Ta)-B_4(Nb,Ta)_2]$, absent of glue atoms. The last cluster $[(Nb,Ta)-B_{12}(Nb,Ta)_6]$ is chosen as the principal cluster for the largest phase formula generated. This is also the only B-rich cluster and is the closest to the phase composition.

B(Nb,Ta) is of the BCr structure and presents $[B-B_2(Nb,Ta)_7]$ and $[(Nb,Ta)-B_7(Nb,Ta)_{10}]$ clusters. The relevant phase formulas are [B-(Nb,Ta)] and [(Nb,Ta)-B], respectively. Like in the BFe structure type, both can be used in interpreting eutectics.

The B-(V,Nb,Ta) eutectics are well explained using the principal clusters from respective eutectic phases (Figs 8–10 and Table 1):



Figure 5. Interpretation of B-Y eutectic points. The dual-cluster formulas come from eutectic phases α -Y-B₂Y, B₂Y-B₄Y, and B₁₂Y-B₆Y.

 $B_{15}V_{85} \rightarrow [V-V_{14} + V-B_4V_{10}]BV_3 = B_5V_{29} \approx B_{14.7}V_{85.3}$ (Fig. 8), where the clusters come from V (W) and B_2V_3 (Si₂U₃);

 $B_{14}Nb_{86} \rightarrow [Nb-B_4Nb_{10} + Nb-Nb_{14}]BNb_5 = B_5Nb_{31} \approx B_{13.9}Nb_{86.1}$ (Fig. 9), where the clusters come from B_2Nb_3 (Si₂U₃) and Nb (W);

 $B_{52}Nb_{48} \rightarrow [Nb-B_{12}Nb_6 + B-B_2Nb_7]Nb_2B_2 = B_{17}Nb_{16} \approx B_{51.5}Nb_{48.5}$ (Fig. 9), where the clusters come from B₄Nb₃ (B₄Ta₃) and BNb (BCr);

 $B_{23}Ta_{77} \rightarrow [B-B_2Ta_8 + Ta-Ta_{14}]B_4 = B_7Ta_{23} \approx B_{23.3}Ta_{76.7} \text{ (Fig. 10), where the clusters come from } BTa_2 \text{ (Al}_2Cu) \text{ and } Ta \text{ (W);}$

 $B_{61}Ta_{39} \rightarrow [Ta-B_{12}Ta_6 + Ta-B_{12}Ta_6]Ta_3B_3 = B_{27}Ta_{17} \approx B_{61.4}Ta_{38.6}$ (Fig. 10), where the clusters come from B_2Ta (AlB₂) and B_4Ta_3 .

The cluster $[B-B_3Ta_6]$ from B_2Ta (AlB₂) cannot give any solutions to the last eutectic. This is also the rare example where the dual cluster formula is constructed from two identical clusters, which indicates that the glue atom matching can also be important. It is noted that the glue atoms Ta_3B_3 cannot be evenly assigned to the identical cluster $[Ta-B_{12}Ta_6]$, so that the resultant cluster formulas for the two liquid subunits are never identical, which is also a common feature for eutectics.

5) VIA elements Cr, Mo, and W

No new structure type appears in the B-Cr system. The eutectics are all well explained (Fig. 11 and Table 1): $B_{13,5}Cr_{86,5} \rightarrow [Cr-Cr_{14} + B-B_2Cr_8]BCr_3 = B_4Cr_{26} \approx B_{13,3}Cr_{86,7}$, where the clusters come from Cr (W) and BCr₂ (Al₂Cu);

 $B_{53,5}Cr_{46,5} \rightarrow [Cr-B_7Cr_{10} + Cr-B_{12}Cr_6]B_4Cr_2 = B_{23}Cr_{20} \approx B_{53,5}Cr_{46,5}$, where the clusters come from BCr and B_4Cr_3 (B_4Ta_3).

The B-richest eutectic $B_{83}Cr_{17}$ cannot be explained with any dual cluster formulas from phase B_2Cr (AlB₂) and β -B.

The B-Mo eutectic is explained by

 $B_{23}Mo_{77} \rightarrow [Mo-Mo_{14} + B-B_2Mo_8]B_4 = B_7Mo_{23} \approx B_{23,3}Mo_{76,7}$ (Fig. 12 and Table 1), where the clusters come from Mo (W) and BMo₂ (Al₂Cu).

 B_5W_2 has the structure type B_5Mo_2 , presenting four clusters, $[B-B_6]$, $[B-B_3]$, $[B-B_6W_4]$, and $[W-B_{13}]$. The relevant phase formulas are respectively $[B-B]W_2B_3$, $[B]WB_{1.5}$, $[B-B_{0.5}W]B$, and $[W-B_{2.5}]$. $[W-B_{13}]$ should be the principal clusters for the absence of glue atoms in the largest phase formula.

Except the B-richest one, all the B-W eutectics are explained as shown in Fig. 13 and Table 1:

 $B_{27}W_{73} \rightarrow [B-W_{14} + B-B_2W_8]B_4 = B_8W_{22} \approx B_{26.7}W_{73.7}$, where the clusters come from W (W, a B-centered prototype has to be adopted) and BW_2 (Al₂Cu);

$$\begin{split} B_{43}W_{57} \rightarrow & [B-B_2W_8 + B-B_3W_7]B_5W = B_{12}W_{16} \approx B_{42.9}W_{57.1}, \\ [B-B_2W_8 + W-B_7W_{10}]B_5W = B_{15}W_{20} \approx B_{42.9}W_{57.1}, \\ \text{where the clusters come } BW_2 \ (Al_2Cu) \ \text{and} \ \beta - BW \ (BCr, \text{ the } W\text{-rich cluster}); \end{split}$$

 $B_{63}W_{37} \rightarrow [B-B_3W_7 + W-B_{13}]W_2 = B_{17}W_{10} \approx B_{63.0}W_{37.0}, \\ [W-B_7W_{10} + W-B_{13}]B_4W_2 = B_{24}W_{14} \approx B_{63.2}W_{36.8}, \\ \text{where the clusters come from } \beta - BW \ (BCr) \text{ and } B_5W_2 \ (B_5Mo_2). \\ \end{cases}$

Notice that in explaining eutectic $B_{27}W_{73}$, the cluster is made B-centered on the basis of the pure metal cluster [W-W₁₄] in order to give a satisfactory explanation. This is different from all other B-metals systems, where the clusters retain the pure metal forms. At present, we are unable to give a sound explanation for this special case.

6) VIIA element Mn

No new structure types are encountered in this system. The eutectics are explained as (Fig. 14 and Table 1):

 $B_{14.3}Mn_{85.7} \rightarrow [Mn-Mn_{14}+B-B_2Mn_8]BMn = B_4Mn_{24} \approx B_{14.3}Mn_{85.7}$, where the clusters come from δ -Mn (W) and BMn₂ (Al₂Cu);



Figure 6. Interpretation of the B-Zr eutectic point. The dual cluster formula comes from eutectic phases B_2Zr and β -Zr.



Figure 7. Interpretation of the B-Hf eutectic point. The dual cluster formula comes from eutectic phases BHf and β -Ti.

 $B_{37}Mn_{63} \rightarrow [B-B_2Mn_8 + B-B_2Mn_7]B_4Mn_2 = [B-B_2Mn_8 + Mn-B_7Mn_6]Mn_2 = B_{10}Mn_{17} \approx B_{37.0}Mn_{63.0}, \mbox{ where the clusters come from } BMn_2 \ (Al_2Cu) \ \mbox{and } BMn \ (BFe);$

 $B_{61.5}Mn_{38.5} \rightarrow [Mn-B_{12}Mn_6 + Mn-B_{12}Mn_6]B_3Mn_3 = B_{27}Mn_{17} \approx B_{61.4}Mn_{38.6}, \text{ where the clusters come from } B_4Mn_3 \\ (B_4Ta_3) \text{ and } B_2Mn \text{ (AlB}_2).$

The last one presents another example where two identical clusters are involved, similar to $B_{61}Ta_{39}$. The B-richest $B_{80}Mn_{20}$ is not explained.

7) VIIIA elements Fe, Co, Ni, and Pd

New structure types are γ -Fe, monoclinic B₃Ni₄, orthorhombic B₃Ni₄, and B₂Pd₅.

 γ -Fe (FCC, Cu type) is characterized by a unique cuboctahedral cluster [Fe-Fe₁₂], typical for FCC metals. The B-Fe eutectics are explained below (Fig. 15 and Table 1):

 $B_{17}Fe_{83} \rightarrow [Fe-Fe_{12} + B-\overline{B}_2Fe_8]B_2Fe_4 = B_5Fe_{25} \approx B_{16.7}Fe_{83.3}$, where the clusters come from γ -Fe (Cu) and BFe₂ (AlCu₂);

 $B_{64,0}Fe_{36,0} \rightarrow [Fe-B_7Fe_{10}+B-B_6]B_6 = B_{20}Fe_{11} \approx B_{64,5}Fe_{35,5}, \text{ where the clusters come from BFe (BFe) and } \beta-B.$

The m- B_3Ni_4 phase contains four clusters, octahedral antiprism [B- B_2Ni_8], capped trigonal prism [B- B_2Ni_7], [Ni- B_6Ni_{10}], and [B- B_5Ni_{10}]. The phase formulas out of these clusters are [B- B_2Ni_4], [B- $B_{0.5}Ni_2$], [Ni- $B_{1.5}Ni$], and [Ni- $B_{1.5}Ni$]. The [B- B_2Ni_8] cluster that leads to the largest formula [B- B_2Ni_4] of seven atoms is taken as the principal cluster.



Figure 8. Interpretation of the B-V eutectic point. The dual cluster formula comes from eutectic phases V and B_2V_3 .



Figure 9. Interpretation of B-Nb eutectic points. The dual cluster formulas come from eutectic phases Nb-B₂Nb and B₄Nb₃-BNb.

The orthorhombic B_3Ni_4 phase contains seven clusters, $[B-Ni_9]$, $[B-B_2Ni_7]$, $[B-B_2Ni_7]$, $[Ni-B_4Ni_{10}]$, $[Ni-B_6Ni_{11}]$, $[Ni-B_7Ni_{10}]$, and $[Ni-B_6Ni_{11}]$, which give respective phase formulas $[B-Ni_4]B_2$, $[B-Ni_3]B_2Ni$, $[B-Ni_3]B_2Ni$, $[B-BNi_4]B_3$, $[Ni-B_3Ni_3]$, $[Ni-B_3Ni_3]$, and $[Ni-B_2Ni_3]B$. The clusters $[Ni-B_6Ni_{11}]$ and $[Ni-B_7Ni_{10}]$ are selected as the principal clusters for the absence of glue atoms in their respective phase formulas.

The B-Ni eutectics are explained as (Fig. 16 and Table 1):

 $\begin{array}{l} B_{17}Ni_{83} \rightarrow [Ni-Ni_{12}+B-Ni_{9}]B_4Ni_2 = B_5\bar{N}i_{24} \approx B_{17.2}Ni_{82.8}, \text{ where the clusters come from Ni (Cu) and BNi_3 (CFe_3); \\ B_{30}Ni_{70} \rightarrow [B-Ni_9+B-B_2Ni_8]B_4Ni_2 = B_8Ni_{19} \approx B_{29.6}Ni_{70.4}, \text{ where the clusters come from BNi}_3 (CFe_3) \text{ and BNi}_2 (AlCu_2); \end{array}$

 $B_{39,5}Ni_{60,5} \rightarrow [B-B_2Ni_8 + Ni-B_6Ni_{11}]B_4 = [B-B_2Ni_8 + Ni-B_7Ni_{10}]B_3Ni = B_{13}Ni_{20} \approx B_{39,4}Ni_{60,6}, \text{ where the clusters come from } BNi_2 \text{ (AlCu}_2) \text{ and } o-B_3Ni_4 \text{ (both principal clusters are used);}$



Figure 10. Interpretation of B-Ta eutectic points. The dual cluster formulas come from eutectic phases BTa₂-Ta and B₂Ta-B₄Ta₃.



Figure 11. Interpretation of B-Cr eutectic points. The dual cluster formulas come from eutectic phases Cr-BCr₂ and BCr-B₄Cr₃.

.....

 $B_{45.3}Ni_{54.7} \rightarrow [B-B_2Ni_8 + Ni-B_7Ni_{10}]B_6 = B_{16}Ni_{19} \approx B_{45.7}Ni_{54.3}, \text{ where the clusters come from } m-B_3Ni_4 \text{ and } BNi (BCr).$

The B₂Pd₅ structure presents four clusters, capped trigonal prism [B-Pd₉], [Pd-B₄Pd₁₂], [Pd-B₄Pd₁₀], and [Pd-B₃Pd₁₁]. The phase formulas expressed by these clusters are respectively [B-Pd_{2.5}], [Pd-BPd_{1.5}], [Pd-B₂Pd₄], and [Pd-BPd_{1.5}]. Among them, [Pd-B₄Pd₁₀] generates the largest phase formula and has a cluster reduction rate of 7/15 \approx 0.47. It is noticed that [B-Pd₉] generates a smaller phase formula of 3.5 atoms, but its cluster reduction rate of 3.5/9 \approx 0.39 is only slightly below that of [Pd-B₄Pd₁₀]. This means that both [Pd-B₄Pd₁₀] and [B-Pd₉] can be the principal clusters. The latter one should be more favored to explain the Pd-rich eutectic. Actually, the [B-Pd₉] cluster gives better explanations for the eutectics than the [Pd-B₄Pd₁₀] does, as shown below (Fig. 17 and Table 1):

 $B_{24,2}Pd_{75,8} \rightarrow [Pd-Pd_{12} + Pd-B_4Pd_{10}]B_4Pd_2 = B_8Pd_{26} \approx B_{23,5}Pd_{76,5}$, where the clusters come from Pd (Cu) and B_2Pd_5 (the composition deviation of -0.9 at.% B being the largest in all the eutectics treated here) or $[Pd-Pd_{12} + B-Pd_9]$ $B_6 = B_7Pd_{22} \approx B_{24,1}Pd_{75,8}$ using the clusters from Pd (Cu) and BPd₃ (CFe₃);

 $B_{34.6}Pd_{65.4} \rightarrow [B-Pd_9 + B-B_6]Pd_6 = B_8Pd_{15} \approx B_{34.8}Pd_{65.2}$, where the clusters come from B_3Pd (CFe₃) and β -B. 8) IVB element C

Only C forms a eutectic type phase diagram with B. There is a carbon boride solid solution zone with a rough B_4C empirical composition. The $B_{13}C_2$ structure presents four clusters, $[B-C_2]$, tetrahedron $[C-B_4]$, pentagonal pyramid $[B-C_5]$, and pentagonal pyramid $[B-B_6]$. It should be noticed that in describing borides, we stick to the principal of nearest-neighbor coordination polyhedron, which leads to the pentagonal pyramids, rather than the B_{12} icosahedron without central atom as normally used in the literature. The phase formula expressed by these



Figure 12. Interpretation of the B-Mo eutectic point. The dual cluster formula comes from eutectic phases Mo and BMo₂.





clusters are respectively $[B-C_2]B_{12}$, $[C-B_{0.5}B_3]B_3$, $[B-B_{7/6}C_{1/3}]$, and $[B-B]B_{1/6}C_{1/3}$. Among them, the $[B-CB_5]$ cluster expresses the phase without using glue atoms and is taken as the principal cluster.

Graphite has a layered hexagonal structure, presenting two identical triangular clusters [C-C₃].

The only eutectic point is explained with the pentagonal pyramid $[B-CB_5]$ from $B_{13}C_2$ and the triangular $[C-C_3]$ from graphite (Fig. 18):

$$B_{71}C_{29} \rightarrow [B - CB_5 + C - C_3]B_6 = B_{12}C_5 \approx B_{70.6}C_{29.4}$$

This B-C system exemplifies the eutectic systems possessing covalent bonding, signifying the universality of the present formulism for binary eutectics.







Figure 15. Interpretation of B-Fe eutectic points. The dual cluster formulas come from eutectic phases Fe-BFe₂ and BFe-B.

Dual cluster formulas of some common binary eutectics

Other eutectics are being examined, and the dual cluster formulas are generally preserved but sometimes modifications on clusters are necessary. A few commonly encountered eutectics involving simple structures and pure metals are attempted below.

 $C_{17.3}Fe_{82.7} \rightarrow [Fe-Fe_{12} + C-Fe_9]C_4Fe_2 = C_5Fe_{24} \approx C_{17.2}Fe_{82.8}$, where the clusters are from γ -Fe (Cu) and CFe₃ (cementite);

 $Cr_{56}Ni_{44} \rightarrow [Ni-Ni_{12} + Cr-Cr_{14}]Cr_4Ni_2 = Cr_{19}Ni_{15} \approx Cr_{55.9}Ni_{44.1}$, where the clusters come from Ni (Cu) and Cr (W);

 $Fe_{29.5}Ti_{70.5} \rightarrow [Ti-Ti_{14} + Fe-Ti_8Fe_6]Fe_3Ti_1 = [Ti-Ti_{14} + Ti-Fe_8Ti_6]Fe_2Ti_2 = Fe_{10}Ti_{24} \approx Fe_{29.4}Ti_{70.6}, \text{ where the clusters come from Fe (W) and FeTi (CsCl, CN14 rhombi-dodecahedral cluster).}$

 $Au_{81,4}Si_{18,6} \rightarrow [Au-Au_{12} + Si-Au_4]Si_3Au_1 = Au_{18}Si_4 \approx Au_{81,8}Si_{18,2}$, where the clusters come from Au (Cu) and Si (diamond type structure, assuming Au substitutions on the shell sites of the CN4 tetrahedral cluster);

 $Sn_{85,1}Zn_{14,9} \rightarrow [Sn-Sn_4 + Zn-Sn_{12}]Zn_2 = Sn_{17}Zn_3 = Sn_{85,0}Zn_{15,0}$, where the clusters come from β -Sn (grey tin, space group 141) and Zn (Mg, assuming Sn substitutions on the shell sites of the CN12 twinned octahedral cluster); $Al_{87,8}Si_{12,2} \rightarrow [Al-Al_{12} + Si-Al_4]Al_4Si_2 = Al_{31}Si_3 = Al_{87,5}Si_{12,5}$, where the clusters come from Al (Cu) and Si (diamond, assuming Al substitutions at the shell sites of the tetrahedral cluster).

 $Ag_{60.1}Cu_{39.9} \rightarrow [Ag-Ag_{12} + Ag-Cu_{12}]Ag_4 = Ag_{18}Cu_{12} = Ag_{60}Cu_{40}$, where the clusters come from Ag (Cu) and Cu (assuming Ag substitution at the center site).

 $Al_{82.9}Cu_{17.1} \rightarrow [Al-Al_{12} + Cu-Cu_2Al_8]Al_4Cu_2 = Al_{25}Cu_5 \approx Al_{83.3}Cu_{16.7}$, where the clusters come from Al (Cu) and Al₂Cu.

In all these interpreted eutectic formulas, the dual cluster form is always retained but the compositions of the pure metal cluster are generally adjusted. At present, the general substitution rules in these pure metal clusters are not completely understood. More examples should be analyzed, which will be the objective of our future research.



Figure 16. Interpretation of B-Ni eutectic points. The dual cluster formulas come from eutectic phases Ni-BNi₃, BNi₃-BNi₂, BNi₂-o-B₃Ni₄, and m-B₃Ni₄-BNi.



Figure 17. Interpretation of B-Pd eutectic points. The dual cluster formulas come from eutectic phases Pd-B₃Pd₂ (or BPd₃) and BPd₃-B.



Figure 18. Interpretation of the B-C eutectic point. The dual cluster formula comes from eutectic phases $B_{13}C_2$ and B.

Properties of eutectic formulas

Except some terminal eutectics by the B side and all those located extremely close to the other sides, normal eutectics in B-containing binary systems are all well explained with dual cluster formulas formed with clusters from relevant eutectic phases plus appropriate glue atoms of 2, 4, or 6. The eutectic formulas, for B eutectics but not limited to, present the following common properties:

1) Eutectic formulas vary extensively, complicated by different cluster geometries and configurations as well as by the matching of different glue atoms. For instance, two identical pairs of clusters $[Co-Co_{12} + B-Co_9]$ and $[Ni-Ni_{12} + B-Ni_9]$, after being matched with different glue atoms, respectively B_4 and B_4Ni_2 , point to two different eutectic compositions $B_{18.5}Co_{81.5}$ and $B_{17}Ni_{83}$. In all the 35 eutectics dealt with here, only two identical eutectic formulas are encountered, $B_7(Ta,Mo)_{23}$ and $B_{27}(Ta,Mn)_{17}$.

2) A eutectic formula is not constructed from two identical subunits. Even for eutectic compositions expressed with identical clusters like $B_{27}(Ta,Mn)_{17} = [(Ta,Mn)-B_{12}(Ta,Mn)_6 + (Ta,Mn)-B_{12}(Ta,Mn)_6]B_3Mn_3$, the two subunits cannot be made identical, because the glue atoms B_3M_3 cannot be evenly assigned to each cluster.

3) Eutectic formulas are generally formed from two distinct types of clusters.

Many cluster types are involved. Common ones are CN9 capped trigonal prisms, CN10 octahedral antiprisms, CN12 octahedra or twinned octahedra, and CN14 rhombi dodecahedra. This fact indicates that cluster matching

plays a dominating and yet unknown role in stabilizing a eutectic liquid, and the distinctly different clusters lead to two eutectic phases of large composition differences. The exceptions are found only for $[(Ta,Mn)-B_{12}(Ta,Mn)_6 + (Ta,Mn)-B_{12}(Ta,Mn)_6]$ (Ta,Mn)-B₁₂(Ta,Mn)₆] (Ta,Mn)-B₁₂(Ta,Mn)₆] (Ta,Mn)-B₁₂(Ta,Mn) - B₁₂(Ta,Mn) - B_{12}(Ta,Mn) - B_{12}(Ta,Mn

Regarding the cluster matching rule, the CN12 clusters from FCC and HCP metals are generally associated with CN9 capped trigonal prisms such as $[B-(Be,Co,Ni,Pd)_9]$ and $[B-B_3(Sc,Y)_6]$. The CN14 clusters from the BCC W structure are matched to more varieties of clusters, but the occurrence of the CN10 octahedral antiprism clusters is the most frequent.

4) Simple integer ratios

In confirmation of Kokandale's eutectic puzzle that eutectics occur near simple composition ratios¹⁰, the present B-containing binary eutectics are especially abundant by composition ratios of 1:6 (the first number representing B number), 1:5, 1:3, 3:5, 3:2, and 5:2 (Table 1), though more eutectics should be treated in order to give a better statistic account of the eutectic distribution.

By unveiling the cluster-based formulism, we have actually developed a new tool for the description of liquid structures, focusing only on their characteristic short-range-order units. Experimental validation of the cluster-based eutectic structures can now be envisaged, which has long been hindered by the lack of a suitable short-range-order structural model. Also, our approach and the formulism thereof may provide a practical composition design method for multi-element eutectic alloys via substitutions of binary eutectic formulas by similar elements.

In conclusion, eutectic structure and composition rule have been addressed using the cluster-plus-glue-atom model for the description of short-range-order structures. It is assumed that a eutectic liquid consist of two different subunits issued from the relevant eutectic phases, each being expressed by the cluster formula for ideal metallic glasses, i.e., [cluster](glue atom)_{1 or 3}. Such a dual cluster formulism is well validated in B-containing eutectics (except those located by the extreme phase diagram ends). The dual cluster formulas vary extensively and are always composed of different subunits. They are generally formed with two distinctly different cluster types, with special cluster matching rules such as cuboctahedron with capped trigonal prism and rhombi-dodecahedron with octahedral antiprism.

References

- 1. Mudry, S., Shtablavyi, I. & Shcherba, I. Liquid eutectic alloys as a cluster solutions. Arch. Mater. Sci. & Eng. 34, 14–18 (2008).
- 2. Pasturel, A. & Jakse, N. Local order and dynamic properties in liquid Au-Ge eutectic alloys by ab initio molecular dynamics. Phys.
- *Rev. B* 84, 134201–134206 (2011).
 Bokhonov, B. & Korchagin, M. *In situ* investigation of stage of the formation of eutectic alloys in Si-Au and Si-Al systems. *J. Alloys & Comp.* 312, 238–250 (2000).
- 4. Pervov, V. S., Mikheikin, I. D., Makhonina, E. V. & Butskii, V. D. Supramolecular assemblies in eutectic alloys. Rus. Chem. Rev. 72, 759–768 (2003).
- 5. Rastogi, R. P. & Bassi, P. S. Mechanism of Eutectic Crystallization. J. Phys. Chem. 68, 2398-2406 (1964).
- Mudry, S., ShtablavyiI. & Shevernoga, I. Structural disordering in Sn-Pb(Bi) eutectic melts induced by heating. Pol. J. Chem. Techn. 15, 61–64 (2013).
- 7. Il'inskii, A., Slyusarenko, S., Slukhovskii, O., Kaban, I. & Hoyer, W. Structure of liquid Fe-Al alloys. Mater. Sci. & Eng. A 325, 98 (2002).
- 8. Neumann, H., Herwig, F. & Hoyer, W. The short range order of liquid eutectic AIII-Te and AIV-Te alloys. J. Non-Cryst. Solids 205-207, 438-442 (1996).
- 9. Sun, J. J., Zheng, H. L., Shi, X. Y. & Tian, X. L. Structure correlation of CoSn eutectic alloy between liquid and solid states. Sci. Chn. Techn. Sci. 52, 3674–3677 (2009).
- Stockdale, D. Numerical Relationships in Binary Metallic Systems. Proc. Roy. Soc. London. Series A, Math. Phys. Sci. 152, 81–104 (1935).
 Frank, F. Supercooling of liquids. Proc. Roy. Soc. London. Series A, Math. Phys. Sci. 215, 43–46 (1952).
- 12. Hume-Rothery, W. & Anderson, E. Eutectic compositions and liquid immiscibility in certain binary alloys. *Philos. Mag.* 5, 383–405 (1960).
- 13. Yavari, A. R. Solving the puzzle of eutectic compositions with 'Miracle glasses'. Nat. Mater. 4, 2-3 (2005).
- 14. Miracle, D. B. A structural model for metallic glasses. Nat. Mater. 3, 697-702 (2004).
- Shi, L. L., Xu, J. & Ma, E. Alloy compositions of metallic glasses and eutectics from an idealized structural model. Acta Mater. 56, 3613–3621 (2008).
- Dong, C. et al. From clusters to phase diagrams: composition rules of quasicrystals and bulk metallic glasses. J. Phys. D: Appl. Phys. 40, R273–291 (2007).
- 17. Hong, H. L., Wang, Q., Dong, C. & Liaw, P. K. Understanding the Cu-Zn brass alloys using a short-range-order cluster model: significance of specific compositions of industrial alloys. *Sci. Rep.* **4**, 7065; doi: 10.1038/srep07065 (2014).
- Luo, L. J. & Dong, C. Comment on "Comparative analysis of glass-formation in binary, ternary, and multicomponent alloys". J. Appl. Phys. 114, 166101 (2013).
- 19. Han, G. et al. The e/a values of ideal metallic glasses in relation to cluster formulae. Acta Mater. 59, 5917–5923 (2011).
- 20. Luo, L. J. et al. 24 electron cluster formulas as the 'molecular' units of ideal metallic glasses. Philos. Mag. 94, 2520-2540 (2014).
- 21. Chen, J. X., Wang, Q., Wang, Y. M., Qiang, J. B. & Dong, C. Cluster formulae for alloy phases. Philos. Mag. Lett. 90, 683-688 (2010).
- Du, J. L., Wen, B., Melnik, R. & Kawazoe, Y. Determining characteristic principal clusters in the "cluster-plus-glue-atom" model. Acta Mater. 75, 113–121 (2014).
- 23. Villars, P. & Calvert, L. D. Pearson's handbook of crystallographic data for intermetallic phases (ASM International 1985).
- 24. Massalski, T. B. (Editor-in-Chief), Okamoto, H., Subramanian, P. R. & Kacprzak, L. (Editors). Binary Alloy Phase Diagrams, Second Edition Plus Updates (ASM International 1990).

Acknowledgements

The present work is supported by Natural Science Foundation of China (51131002), Natural Science Foundation of Hainan Province (514203), and Key Scientific & Technological Project of Hainan Province (ZDZX2013002).

Author Contributions

Y.P.M, D.D.D. and L.J.L. collected and analyzed the eutectic composition and structure data. C.D. proposed the model. Q.W, J.B.Q. and Y.M.W. helped with composition interpretation. All authors participated in writing the paper.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Ma, Y. P. *et al.* Composition formulas of binary eutectics. *Sci. Rep.* **5**, 17880; doi: 10.1038/srep17880 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/