Compositions design of Co-Fe-based bulk metallic alloys

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Keywords: bulk metallic glass, compositions design, Co-Fe based alloys, amorphous alloys

Abstract
Glass forming ability (GFA) is one of the key factors hindering the application of bulk metallic glasses (BMGs). In this paper, a cluster-related method was used to design good glass-formers in the complex Co-Fe-based system. A novel Co-centered Co-Mo binary topologically packed cluster Co-Co8Mo4 with 12-coordination number was found and used. The basic ternary composition in Co-Mo-B system is calculated based on an intersection of cluster lines B-B2Co8 and Co-Co8Mo4. Based on this, a series of novel Co-Fe-based glass-formers with high GFA, were quickly designed using the method of similar element replacement and microalloying. The best glass-former is (Co27.5Fe27.5Mo12.2Cr12.2B16P4.6)98Y2. The source of high GFA of designed glass-formers was also discussed. The results of this paper would offer researchers a novel insight in understanding the source of high GFA of Co/Fe-based system, and lay a solid foundation for exploring Co/Fe-Mo-based glass-formers via newly found Co-Mo binary cluster.

1. Introduction
In the family of bulk metallic glasses (BMGs), Co-Fe-based amorphous alloys have attracted a lot of attention, owing to their super mechanical properties, unique magnetic properties, remarkable low materials lost and great corrosion resistance [1–7]. Considering these superb properties, Co-Fe-based BMGs have an excellent application prospect. Meanwhile, limited glass-forming ability (GFA) often acts as the role of limiting the scope of application [8, 9]. Due to the sensitivity of GFA to compositions, it is always a big challenge to discover new glass-formers with high GFA.

It is through decades of hard work that some novel Co-Fe-based glass-formers with high GFA have been developed [2, 3, 5, 10]. For example, by the method of drop casting in Cu mould, Fe41Co7Cr15Mo14C15B6Y2 could be fabricated into a fully amorphous rod with a critical diameter of 16 mm [10]. However, to sum up, most of the found Co-Fe-based glass-formers were developed according to the empirical law. In the field of research on GFA of Co-Fe-based BMGs, there were few research papers, especially from the aspect of microstructure, which would lay a foundation for further understanding glass-formation and enhancing GFA.

In order to understand glass-formation and design good glass-formers with high GFA, a lot of methods have been proposed from different points of view, such as from the aspect of microstructure or thermodynamics [11–16]. For example, based on the feature of microstructure, Miracle has proposed an efficient close packing (ECP) model, which has showed a great success in understanding glass formers and glass formation [14, 15]. Thermodynamics also plays important role in understanding and designing glass-formers. Researchers have designed a series of novel high-entropy metallic glass-formers only from the aspect of entropy of mixing [17–19]. Meanwhile, some methods based on combining microstructure and thermodynamics also work well in
developing Zr-based glass-formers [9, 11, 20]. All of the above methods have achieved certain success in different fields.

From the aspect of microstructure, a novel cluster-related model named cluster-glue-atom model has been proposed by Chuang Dong [21–24]. This method showed great success in understanding and designing good glass-formers in Fe-based, Ni-based and rare-earth-based and Zr-based systems, etc [13, 25, 26]. Under the guidance of this cluster-glue-atom model, glass-formers were treated as isolated clusters plus glue atoms. The ratio of isolated clusters to glue atoms in a certain glass-former is always 1:1 or 1:3 [13]. This cluster-glue-atom model is a very efficient method of understanding complex glass-formers and designing good glass-formers with high GFA.

In this work, firstly, Co-Fe-based glass-formers have been understood via similar elements replacement and mixing enthalpy. Secondly, a novel Fe-Mo-based binary cluster was found and used as the basic cluster, which expanded the database of present binary clusters, laying a solid foundation for further developing Co-Mo-based glass-formers. At last, under the guidance of cluster-plus-glue-atom model, a series of novel Co-Fe based glass formers with high GFA have been understood and designed.

2. Experiment

2.1. Compositions design

In this work, Co-Fe-Mo-Cr-P-B-(Y) was chosen as the basic system to study the glass-formation in Co-Fe-based alloys. Co, Fe, Mo, Cr, P, B and Y are chosen as the basic elemental compositions in Co-Fe-based alloys due to the reasons below: (1) The atomic radiuses, atomic size difference and heat of mixing between each elements meet the requirement of Inoue’s empirical law, which means potential high GFA [27]. (2) The best glass formers in Fe-based and Co-base glassy alloys locate at Fe₄₁Co₇Cr₁₅Mo₁₄C₁₅B₆Y₂ and Co₄₈Cr₁₅Mo₁₄C₁₅B₆Er₂, respectively [10, 28, 29]. It can be seen that, Mo, Cr, C, B and rare-earth element are the main elements in the above best Fe-best and Co-best glass-formers. According to the literature, P was also one of the common constitute elements in Fe/Co based glassy alloys, such as in (Fe-Co-Ni)-P-C-B, etc [1]. The results show that P element was also beneficial to GFA in Co-Fe based alloys. Based on this, C was replaced by P and Y was chosen as the candidate of rare-earth elements. On the other hand, the study on glass-formation of (Co-Fe)-(Mo, Cr)-(P, B)-Y system is limited. Under the guidance of Dong’s cluster-related method, in the field of research on the GFA of (Co-Fe)-(Mo, Cr)-(P, B)-Y system, a series of novel Co-Fe-based glass-formers with high GFA would be found, which might lay a foundation of understanding the source of high GFA of Fe₄₁Co₇Cr₁₅Mo₁₄C₁₅B₆Y₂ and Co₄₈Cr₁₅Mo₁₄C₁₅B₆Er₂, and further guide researchers to enhance GFA of Co-Fe-based amorphous alloys.

To study the GFA of the complex system of Co-Fe-Mo-Cr-P-B-Y, the first step is simplifying the system. Firstly, rare earth Y always plays the role as micro-alloying element, which could further enhance the GFA of basic system, such as in Fe-based, Cu-based and Zr-based amorphous system, etc [30]. So, Y was also regarded as the micro-alloying element in this Co-Fe-based system. Secondly, Miracle once pointed that, similar elements might replace each other’s location in cluster’s shell [14, 15]. In this system, the radius of Co and Fe are 0.125 nm and 0.128 nm, respectively. They share similar location in the periodic table and enjoy similar chemical properties. So, Co and Fe could be regarded as similar elements. Similarly, Mo/Cr and P/B could be also regarded as similar elements. Based on the above analysis, this complex system Co-Fe-Mo-Cr-P-B-Y could be simplified as Co/Fe-Mo/Co/P-B-microalloying element Y. Further ignoring the microalloying element and considering similar element, the pseudo-ternary Co-Mo-B system could be regarded as the basic system of Co-Fe-Mo-Cr-P-B-Y.

In the pseudo-ternary Co-Mo-B system, considering the content of Co is much higher than Mo and B, Co has more opportunities to form clusters. The enthalpies of mixing of binary pairs Co-Mo and Co-B at equiatomic composition are respectively −5 kJ mol⁻¹ and −24 kJ mol⁻¹ [31]. The negative enthalpy means Co tends to form clusters between B and Mo during the rapid cooling process.

According to the above analysis, Co-B and Co-Mo are more favored to form together. In Co-B binary pair, Zhu has analyzed Co-B crystalline phases, and chosen a series of Co-B binary clusters [32]. Among the clusters, the B-centered archimedean octahedral anti-prism cluster B₂Co₉ was the most topologically packed. Its coordination number (CN) is 10. This cluster has been proven to be successful in designing Co-based system [32]. Therefore, B₂Co₉ was chosen as the representative cluster in Co-B binary system.

It has been demonstrated that, the local structure of amorphous alloys is similar to the microstructure of competing phases [14]. In Co-Mo binary system, there exists four crystalline phases, namely, Co₃Mo₉ (CrFe type), Co₃Mo (Ni₃Sn type), Co₇Mo₆ (Fe₆W₆ type) and CoMo (Mg type). After analyzing, a novel CN12 cluster Co-centered Co-C₀₂₋₅Mo₉ cluster was derived from phase Co₃Mo. The image of cluster Co-C₀₂₋₅Mo₉ is shown in figure 1. However, the cluster should meet the requirement of topological packing. In terms of certain number of CN, Miracle has calculated the best radius ratio (the radius of atom in the center of cluster to the average radius
of atoms in the shell of cluster) [15]. As for the cluster Co-Co$_8$Mo$_4$, the center atom is Co. There exist twelve atoms in this cluster’s shell, namely eight Co atoms and four Mo atoms. The Goldschmidt radiuses of Co and Mo are 0.125 nm and 0.140 nm. The average radius of atoms in Co-Co$_8$Mo$_4$ cluster’s shell is 0.962. As for the CN 12 cluster, the best ideal radius ratio is 0.902 [15]. Based on this, the deviation between the actual and ideal radius ratio is 6.65%. Co-Co$_8$Mo$_4$ could be regarded as a topologically packed cluster, due to the reason that its deviation is less than 10% [15]. Therefore, Co-Co$_8$Mo$_4$ was chosen as the representative cluster in Co-Mo binary system.

In the ternary Co-Mo-B system, two binary clusters B-B$_2$Co$_8$ and Co-Co$_8$Mo$_4$ were shown in figure 2. Based on the cluster-glue-atom model, the cluster line method was always used to design compositions. The best glass-former always locates at the intersection point of two binary clusters.

As can be in figure 2, the glass-former Co$_{35}$Mo$_{24.4}$B$_{20.6}$ is calculated based on an intersection of cluster lines B-B$_2$Co$_8$ and Co-Co$_8$Mo$_4$. It has been proven that similar element replacement could greatly enhance GFA of the basic system. According to the above analysis, Co/Fe, Mo/Cr and B/P could be regarded as similar elements. Hence, half content of Co and Mo were replaced by Fe and Cr, separately. Through this step, a pseudo-ternary Co/Fe-Mo/Cr-B glass-former Co$_{27.5}$Fe$_{27.5}$Mo$_{12.2}$Cr$_{12.2}$B$_{20.6}$ could be designed. Considering high-content P-containing composition was hard to fabricate in industry, thus, little mount of P, namely 4.6 at% P was further replaced by B. Co$_{27.5}$Fe$_{27.5}$Mo$_{12.2}$Cr$_{12.2}$B$_{16}$P$_{4.6}$ was designed. Miro-alloying also plays important role in
enhancing GFA. Thus, 2 at% rare-earth element Y was further micro-alloyed to Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6}, namely, (Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6})_{98}Y_{2}.

2.2. Experimental

In this paper, the purities of Co, Fe, Mo, Cr, B, P and Y are all high. Their purities are: Co (99.99 pure), Fe (99.9 pure), B (99.9 pure), P (99.9 pure), Cr (99.99 pure), and Y (99.5 pure). B and P were first premelted Fe–B and Fe–P binary intermediate alloys. B and P in the compositions were added by Fe–B and Fe–P intermediate alloys. All of the above designed alloys were prepared by means of arc melting. The ingots were fabricated in a titanium-gettered Ar atmosphere. The above Co–Fe-based ingots are at least remelted 3 times to insure the compositional homogeneity. The ribbon of composition Co_{55}Mo_{24.4}B_{20.6} was fabricated by melt spinning. The size of Co–Mo–B ribbon is about 0.02 mm × 1.2 mm. The rod samples are fabricated by Cu mold casting. The diameters of rod samples are 2 mm, 3 mm and 4 mm. The structure of fabricated samples was examined by x-ray diffraction (XRD). The thermodynamic parameters were evaluated using differential scanning calorimetry (Netzsch DSC 404C) at a heating rate of 0.33 K s^{-1} in a flowing purified argon atmosphere.

3. Results and discussion

The XRD patterns of designed compositions are shown in figure 3. As can be seen, there exist unknown phases peaks in XRD pattern of Co_{55}Mo_{24.4}B_{20.6}. It couldn’t form a full amorphous ribbon. The GFA of original designed ternary composition Co_{55}Mo_{24.4}B_{20.6} is quite low. In contrast, there doesn’t exist any shark crystalline peaks in the XRD patterns of Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{20.6}, Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6} and (Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6})_{98}Y_{2}, which means the samples are fully amorphous.

As analyzed above, the designed compositions could be understood by cluster-plus-glue-atom model, namely, [cluster]_{x}[glue atom]_{3}, x = 1 or 3 [12]. Based on this model, the primary ternary composition Co_{55}Mo_{24.4}B_{20.6} could be expressed as the cluster formula [B_{3}Co_{8}-Mo_{3.5}. The glue number is 3.5, which has a small deviation from the theoretical value of 3. The deviation might be the reason of the poor GFA of Co_{55}Mo_{24.4}B_{20.6}.

The critical diameter of Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{20.6}, Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6} and (Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6})_{98}Y_{2} is 2 mm, 3 mm and 4 mm, respectively. It can be seen that, both similar elements replacement and microalloying could greatly enhance GFA. Among our designed compositions, the best glass-former is (Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6})_{98}Y_{2}. The GFA of (Co_{27.5}Fe_{27.5}Mo_{12.2}Cr_{12.2}B_{16}P_{4.6})_{98}Y_{2} is lower than typical Co–Fe-based glass-formers containing with element C. However, its GFA is higher than other Co–Fe-based glass-formers reported in literature, e.g., Fe_{10}Co_{50}Ni_{15}P_{10}C_{10}B_{5} (Dc = 2.5 mm) [1], Fe_{79}Co_{10}P_{13}C_{7} (Dc = 2.5 mm) [33], Fe_{66}Co_{10}Nb_{2}B_{2}Y_{3} (Dc = 3 mm) [2] and Fe_{53}Co_{27}Mo_{5}P_{4}B_{6} (Dc = 3 mm) [33].

As for the enhancement of GFA by similar element replacement, the reasons can be explained by the increase in mixing entropy. It has been reported that, on the precondition of meeting the requirement of topologically
packed in clusters, the more mixing entropy the system possesses, being less likely to crystallize, the higher GFA would reach \[ 11 \]. Elements would replace its similar element’s position in the cluster formula. Based on this, $\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{20.6}, \text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}$ could be expressed in the cluster formula $[\text{B}_3\text{Co}_4\text{Fe}_4]\text{Mo}_{1.75}\text{Cr}_{1.75}$ and $[\text{B}_{2.33}\text{P}_{0.67}\text{Co}_4\text{Fe}_4]\text{Mo}_{1.75}\text{Cr}_{1.75}$.

Y-microalloying could also enhance the GFA of Co-Fe-based alloys, it might be caused by rare-earth element doping could decrease the oxygen impurity concentration \[ 30 \]. In addition, due to the fact that the enthalpy of mixing of binary pairs Fe-Y at equiatomic composition is $-1 \text{ kJ mol}^{-1} \[ 31 \]. There exist amounts of topological clusters, e.g., a Fe-centered CN12 Fe-Fe$_{11}$Y cluster \[ 34 \]. With Y-doping, the newly introduced topological cluster would greatly increase the difficulty in crystallization, which is beneficial for glass-formation.

A series of crystallization behaviors of as-cast $\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{20.6}, \text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}$ and $[\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}]_9\text{Y}_2$ metallic alloys were shown in figure 4. The heating rate is 0.33 K/s. The glass transition temperatures ($T_g$) of $\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{20.6}, \text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}$ and $[\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}]_9\text{Y}_2$ are separately 805 K, 817 K and 785 K. The crystallization temperatures ($T_x$) are separately 864 K, 855 K and 877 K. The supercooled liquid regions $\Delta T$ of the above three amorphous alloys are separately 59 K, 38 K and 102 K. It can be seen that, $\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{20.6}$ and $\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}$ are close to eutectic point. With the micro-alloying Y doped, the crystallization behavior has changed, and the new Y-doped composition possesses the largest undercooled liquid region among our designed compositions in Co-Fe-based metallic alloys. This wide undercooled liquid region and its high GFA would lay a foundation for further fabrication and application.

4. Conclusion

A novel Co-Mo binary topologically packed cluster Co-Co$_8$Mo$_4$ was found and used. Based on cluster line method, a series of novel Co-Fe-based glass-formers with high GFA were quickly designed, combining with similar element replacement and microalloying. Among the designed glass-formers, $[\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}]_9\text{Y}_2$ owes the largest and undercooled liquid region. This glass-former is designed based on an intersection of cluster lines B-B$_2$Co$_8$ and Co-Co$_8$Mo$_4$. The critical diameter of $[\text{Co}_{27.5}\text{Fe}_{27.5}\text{Mo}_{12.2}\text{Cr}_{12.2}\text{B}_{16}\text{P}_{4.6}]_9\text{Y}_2$ is 4 mm. The results in this paper offer the researchers a novel insight in understanding the source of high GFA of Co/Fe-based system, and lay a solid foundation for exploring Co/Fe-Mo-based glass-formers via newly found Co-Mo binary cluster.

Acknowledgments

This work was supported by the Natural Science Foundation of Liaoning Province (Grant No. 20170540453) and open fund project of Shandong Provincal Key Laboratory of Ocean Engineering, Ocean University of China (No. kloe201901).
Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Zhang W, Miao H T, Li Y H, Chang C T, Xie G Q and Jia X J 2017 Glass-forming ability and thermoplastic formability of ferromagnetic (Fe, Co, Ni)$_7$P$_{10}$C$_{10}$B$_5$ metallic glasses J. Alloy. Compd. 707 57–62
[2] de Lucena F A, Kiminami C S and Afonso C R M 2020 New compositions of Fe-Co-Nb-B-Y BMG with wide supercooled liquid range, over 100 K J. Mater. Res.-Techol.-JMRK. 9 9174–81
[3] Aihemaiti N, Li Q, Li M C, Wang T, Chang C T and Ma X 2020 Preparation and properties of CoFeMoO$_6$B$_5$P$_3$ bulk metallic glasses Intermetallics 123 6
[4] Wang S W, Li Y H, Wang X W, Yamaura S and Zhang W 2017 Glass-forming ability, thermal properties, and corrosion resistance of Fe-based (Fe, Ni, Mo, Cr)-P-C-B metallic glasses J. Non-Cryst. Solids 475 75–80
[5] Han Y, Ding J, Kong F, Inoue A, Zhu S, Wang Z, Shalaan E and Al-Marzouki F 2017 FeCo-based soft magnetic alloys with high B-s approaching 1.75 T and good bending ductility J. Alloy. Compd. 691 364–8
[6] Miao H T, Chang C T, Li Y H, Wang Y M, Jia X J and Zhang W 2015 Fabrication and properties of soft magnetic Fe-Co-Ni-P-C-B bulk metallic glasses with high glass-forming ability J. Non-Cryst. Solids 421 24–9
[7] Wu Y X, Li X and Li SL 2020 Crystallization kinetics and soft magnetic properties of Fe$_7$Si$_{0.6}$B$_{0.4}$Cu$_{0.6}$Nb$_{0.2}$ amorphous alloys Mater. Res. Express 7
[8] Li X, Qin C, Kato H, Makino A and Inoue A 2011 Mo microalloying effect on the glass-forming ability, magnetic, mechanical and corrosion properties of (Fe$_{70}$Si$_{10}$B$_{10}$)(Fe$_{20}$P$_{10}$C$_{10}$B$_{5}$) bulk glassy alloys J. Alloy. Compd. 509 7686–91
[9] Yu D, Qin Z, Song Q, Zhang Y and Yuan G 2021 Formation of a Ni- and Be-free Zr-based glassy alloy in centimeter scale Mater. Lett. 288 129383
[10] Shen J, Chen Q J, Sun J F, Fan H B and Wang G 2005 Exceptionally high glass-forming ability of an FeCoCrMoCBY alloy Appl. Phys. Lett. 86 151907
[11] Yu D C, Geng Y, Li Z K, Liu D M, Fu H M, Zhu Z W, Qi Y and Zhang H F 2015 A new method locating good glass-forming compositions J. Alloy. Compd. 646 620–5
[12] Han G, Qiang J, Li F, Yuan L, Quan S, Wang Q, Wang Y, Dong C and Haeussler P 2011 The e/a values of ideal metallic glasses in relation to cluster formulae Acta Mater. 59 5917–23
[13] Naz G J and Dong C 2018 Cluster-plus-glue-atom formulas of Fe-B-based metallic glasses Intermetallics 99 35–8
[14] Miracle D B 2004 Efficient local packing in metallic glasses Journal Of Noncrystalline Solids. 342 89–96
[15] Miracle D B, Sanders W S and Senkov O 2003 The influence of efficient atomic packing on the constitution of metallic glasses Philos. Mag. 83 2409–28
[16] Nagel S and Tauc J 1975 Nearly-free-electron approach to the theory of metallic glass alloys Physical Review Letters - PHYS REV LETT. 35 380–3
[17] Takeuchi A, Chen N, Wada T, Yokoyama Y, Kato H, Inoue A and Yeh J W 2011 Pd$_{20}$Pt$_{20}$Cu$_{20}$Ni$_{20}$P$_{20}$ high-entropy alloy as a bulk metallic glass in the centimeter Intermetallics 19 1546–54
[18] Gao X Q, Zhao K, Ke H B, Ding D W, Wang W and Bai H Y 2011 High mixing entropy bulk metallic glasses J. Non-Cryst. Solids 357 3557–60
[19] Ma L Q, Wang L M, Zhang T and Inoue A 2002 Bulk glass formation of Ti-Zr-Hf-Ta bulk glassy alloys Journal Of Noncrystalline Solids. 277 80–80
[20] Yu D C, Shi X G, Fu H M, Geng Y, Zhu Z W, Qi Y and Zhang H F 2015 Glass formation in Zr-Al-Cu system Mater. Lett. 157 299–302
[21] Wang Z, Dong D, Zhang S, Ma Y and Dong C 2016 Characteristics of cluster formulae for binary bulk metallic glasses J. Alloy. Compd. 654 340–3
[22] Dong D, Zhang S, Wang Z, Dong C and Haeussler P 2016 Composition interpretation of binary bulk metallic glasses via principal cluster definition Mater. Des. 96 115–21
[23] Li F W, Qiang J B, Wang Q, Wang Y M, Dong X L, Dong C and Zhu S J 2012 Best metallic glass former Al$_2$Ni$_2$Zr$_2$ optimized by cluster-plus-glue-atom model Intermetallics 30 866–9
[24] Chen J, Wang Q, Wang Y, Qiang J, Li F, Zhu C and Dong C 2012 Cluster formulae for metallic glasses derived from devitrification phases Philos. Mag. 92 1400–19
[25] Zhu C L, Wang Q, Zhao Y J, Wang Y M, Qiang J B and Dong C 2010 Ni-based Ni-Fe-B-Si-Ta bulk metallic glasses Sci. Phys. Mech. Astron. 53 480–4
[26] Wu J, Wang Q, Chen W, Zhang Q, Qiang J and Dong C 2007 Glass formation of ternary Sm-based Sm-Al-Co bulk metallic glasses Journal of University of Science and Technology Beijing. 14 50–3
[27] Inoue A 2000 Stabilization of metallic supercooled liquid and bulk amorphous alloys Acta Mater. 48 279–306
[28] Men H, Pang S J and Zhang T 2007 Thermal stability and microhardness of new Co-based bulk metallic glasses Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct. Process. 449 538–50
[29] Men H, Pang S J and Zhang T 2006 Effect of Er doping on glass-forming ability of Co$_{80}$Cr$_{10}$Mo$_{10}$C$_{10}$B$_{5}$ alloy Mater. Sci. Eng. 21 938–61
[30] Lu Z P and Liu C T 2004 Role of minor alloying additions in formation of bulk metallic glasses: a review J. Mater. Sci. 39 3965–74
[31] Takeuchi A and Inoue A 2005 Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element Mater. Trans. 46 2817–29
[32] Wang Q, Zhu C, Li Y H, Wu J, Dong C, Qiang J, Zhang W and Inoue A (ed) 2007 Cluster-based bulk metallic glass formation in Co-
Fe-Si-B-Nb alloy systems 6th Pacific Rim Int. Conf. on Advanced Materials and Processing (2007 Nov 05–09) (Cheju Isl, SOUTH
KOREA) (DURNTEN-ZURICH: Trans Tech Publications Ltd)

[33] Xu K, Lin H B, Li Q, Li F, Yao K F and Guo S F 2014 Effects of Co substitution for Fe on the glass forming ability and properties of
Fe80P13C7 bulk metallic glasses Intermetallics 51 53–8

[34] Pemberton-Pigott N, Wang Q, Chen W, Zhang Q, Wu J, Li Y, Qiang J and Dong C 2007 A cluster line approach to finding new Fe-B-Y-
Nb-Zr bulk metallic glasses Journal of University of Science and Technology Beijing. 14 26–30