Understanding the beneficial microalloying elements in Fe-based bulk metallic glasses via clusters

DeChuan Yu1,2∗, YuanXiang Zhang3, Xue Li1,∗ and Guo Yuan1,∗

1. Introduction

Bulk metallic glasses (BMGs) have attracted specific attention due to their unique combination of excellent magnetic properties, mechanical properties and corrosion resistance, showing good practical application prospect [1]. However, glass-forming ability (GFA) is one of the key factors hindering the practical application. It is of great theoretic and actual significance to design good glass formers with high GFA.

It has been reported that minor alloying techniques have obviously shown beneficial effects on enhancing GFA [2, 3]. A lot of research has been done and understood from the aspect of thermodynamics [4, 5]. However, a common conclusion has been reached that the microalloying element should have the tendency of compound formation, namely, the microalloying element should have negative enthalpy of mixing between the major element [2, 3, 6]. Unfortunately, the mechanism of the minor alloying is still unclear. For example, non-metallic elements C, B and Si enjoying a large negative enthalpy of mixing between Fe or Zr element, both of which completely accords with the experience law [6]. However, the results show that these non-metallic elements could obviously enhance the GFA of Fe-based BMGs and deduce the GFA of Zr-based BMGs [7–9]. It is obvious that the negative heats of mixing between the major element is not the determining factor influencing GFA. It is still requiring a large number of experiments which might take a lot of time and money to choose minor alloying element.

How to understand the origin of GFA is always a hot topic in research of amorphous alloys. As cluster is the basic microstructural unit, based on this, some cluster-based methods have been proposed and used to understand and design good glass-formers [10–14]. The results prove that these cluster-based methods show the advantages of understanding and quickly designing glass-formers with high glass-forming ability. Recently, a method combining clusters and mixing entropy was applied by authors and used to understand and design good glass formers [14–17]. Based on it, in this paper, a new guidance via clusters was applied to understand and choose the beneficial microalloying elements. Furthermore, a series of beneficial microalloying elements in Fe-based system were quickly discovered, verified and understood.

© 2021 The Author(s). Published by IOP Publishing Ltd
Here, According to our previous study, the critical diameter of the basic composition Fe$_{76}$Si$_{9.6}$B$_{8.4}$P$_{6}$ is 2.5 mm under 3. Results and discussion

Among the Fe-based glass-formers, Fe$_{76}$Si$_{9.6}$B$_{8.4}$P$_{6}$ has a high saturation magnetization 2. Experiment

least 3 mm, however, 2 at.% V couldn’t work well in the aspect of enhancing GFA for the basic Fe-based glass-former. To test this hypothesis more precisely, more varying amounts of microalloying element V, namely, 1, 2, 3, 4 at.% V were also fabricated and tested. As can be seen in 2, at.%C and Ta enhances GFA from 2.5 mm to at

As shown in table1 and fi
gures 1, it can be seen that GFA is sensitive to the microalloying elements. Even for elements with the same characteristics, all of which enjoy large enthalpy of mixing between the element and the former. To test this hypothesis more precisely, more varying amounts of microalloying element V, namely, 1, 2, 3, 4 at.% V were also fabricated and tested. As can be seen in

As shown in table 1 and fi
gures 1, it can be seen that GFA is sensitive to the microalloying elements. Even for elements with the same characteristics, all of which enjoy large enthalpy of mixing between the element and the major element, it was found that there exists huge discrepancy among the microalloying elements in the field of enhancing GFA.

Understanding the origin of GFA of basic composition is the basis, and should always come before understanding the origin of enhancing GFA by microalloying elements. The enthalpies of mixing of the atomic pairs Fe–Si, Fe–B, Fe–P, Si–B, Si–P and B–P at equiatomic compositions are respectively −35 KJ mol$^{-1}$, −26 KJ mol$^{-1}$, −39.5 KJ mol$^{-1}$, −14 KJ mol$^{-1}$, −25.5 KJ mol$^{-1}$ and 0.5 KJ mol$^{-1}$ [6]. It can be easily concluded that, among the six atomic pairs, Fe–Si, Fe–B and Fe–P clusters are more apt to accumulate as they enjoy more negative enthalpies of mixing than others. Under the guidance of clusters- and mixing entropy-related method, the glass former could be understood as a mixture of efficiently topologically packed clusters [14–16].

The glass former (C$_{am}$) in this system should be written as:

$$C_{am} = \alpha [\text{cluster (Fe–Si)}] + \beta [\text{cluster (Fe–B)}] + \gamma [\text{cluster (Fe–P)}]$$

Here, α, β and γ are coefficients.
It has been reported that there exist efficiently topological packed clusters in Fe–Si and Fe–B binary system, such as cluster B-B2Fe8, Si-Fe9 and P-Fe9, etc [20, 21]. Composition with good GFA in Fe–Si–B–P system could be regarded as a mixture of Fe–Si, Fe–B and Fe–P binary clusters. The topologically efficiently packed clusters could hinder the precipitation of crystalline phases which leads to the high GFA in this system. Based on the analysis above and equation (1), the high GFA in Fe–Si–B–P system comes from the topological packed clusters.

Clusters are the key factors of influencing GFA and further understanding the mechanism of enhancing GFA by microalloying elements. The large enthalpy of mixing between elements is the origin of clusters. As mentioned above, all of the chosen microalloying elements have negative heats of mixing between the major element Fe which is consistent with previous empirical rules [2, 3, 6]. However, the microalloying element V which also enjoys negative heat of mixing between Fe doesn’t work in the field of enhancing GFA. It can be concluded that, the microalloying element enjoying negative heats of mixing between the major element is not the determining factor enhancing GFA such as the microalloying element V in this paper. There exist deeper causes that affect the glass-forming ability via microalloying.

Gaskell and Miracle have pointed that, the local structure of amorphous alloys is similar to the microstructure of the competing phases [13, 22]. This cluster selection rule has been successfully used in designing and understanding good glass-formers [14, 16, 20]. Clusters come from the large enthalpy of mixing between components. All of micro-alloying elements C, Mo, Ta and V enjoy large enthalpy of mixing between the element and the major component Fe. However, among the Fe–M (M = C, Mo and Ta) binary system, after carefully analyzing the microstructure of Fe-based binary competing phases, only binary clusters C-Fe9 (derived from phase CFe3), Fe-Fe4M8 (M = 0.25Fe + 0.75Mo) (derived from phase FeMo) and Fe-Fe6Ta6 (derived from phase Fe2Ta) could be obtained in each corresponding binary system.

It is worth noting that, Miracle once further pointed that, the degree of efficient packing in clusters, which was linked to the radius ratio, plays important role in glass formation [23]. In terms of coordination number (CN) for the certain cluster, the ideal radius ratio $R^*$ has been calculated [23].

![Figure 1. XRD patterns of samples obtained from as-cast alloys with diameter of 2.5 mm and 3 mm.](image1)

![Figure 2. Images of clusters (a): Cluster C-Fe9 derived from phase CFe3, (b): Cluster Fe-Fe4(0.25Fe + 0.75Mo)8 derived from phase FeMo, (c): Cluster Fe-Fe6Ta6 derived from phase Fe2Ta.](image2)
CN12 is 0.710 and 0.902 [23]. The Goldschmidt radius of Fe, C, Mo and Ta is respectively 0.128 nm, 0.77 nm, 0.140 nm and 0.147 nm. The actual radius ratio R is decided by atomic radius of center atom of the cluster and the average atomic radius of atoms in the cluster’s shell. For example, as for the cluster Fe-Fe₄M₈ (M = 0.25Fe + 0.75Mo), the atomic radius of center atom of this cluster is 0.128 nm, and the average atomic radius of atoms in the cluster’s shell is 0.134 nm. Thereby, the actual radius R in cluster Fe-Fe₄M₈ (M = 0.25Fe + 0.75Mo) equals 0.128 nm divided by 0.134 nm, namely 0.955. Similarly, the actual radius ratio R in cluster C-Fe₉, Fe-Fe₄M₈ (M = 0.25Fe + 0.75Mo) and Fe-Fe₆Ta₆ is respectively 0.602, 0.955 and 0.931. The percent difference Δ between R and R* is respectively −15.2%, 5.9% and 3.2%. These clusters are quite close to the requirement of efficiently topologically packed which means beneficial microalloying elements equals introducing new topological clusters. From a thermodynamic point of view, topological clusters would enhance the viscosity of alloy melt increasing the difficulty of rearrangement of atoms. From an energy point of view, the efficiently topologically packed clusters would decrease the thermodynamics free volume of system, which would also simultaneously increase the stability of microstructure. To sum up, beneficial microalloying elements should be chosen under the condition of bringing in new type of topologically efficiently packed clusters rather than enjoy negative heats of mixing between the major element.

The schematic diagram of understanding and choosing the beneficial microalloying elements in Fe-based bulk metallic glasses via clusters is shown in figure 3. The microalloying elements should have negative heat of mixing between the major element Fe. However, from the aspect of clusters, this type could be further subdivided. For some of the microalloying elements, such as V, which also has negative heat of mixing between the major element Fe, however, there doesn’t exist specific clusters in Fe-V binary system. Under the guidance of method related clusters and mixing entropy reported in Refs, the GFA is quite related to microstructure. And cluster is the basic structure unit of BMGs. Microalloying with V would not bring in new type of clusters. Those microalloying elements, having negative heat of mixing between the major element, failing to bring in specific cluster, are categorized as Type 1, such as V etc. element in Fe-based system. Conversely, those microalloying elements, having negative heat of mixing between the major element, bringing in specific cluster, are be categorized as Type 2, such as C, Mo and Ta etc. elements in Fe-based system. The newly introduced type of efficiently topologically packed clusters would increase the number of clusters, leading to a higher entropy of mixing, adding the difficulty of precipitation of crystalline phases, and enhance the original system’s GFA.

4. Conclusion

To sum up, to further enhance GFA, new type of topologically efficiently packed cluster is welcome. That’s to say, beneficial microalloying elements for enhancing GFA should be chosen under the condition of bringing in new type of topologically efficiently packed clusters rather than simply enjoy negative heats of mixing between the major element.

In this paper, a new guidance via clusters was applied to understand and choose the beneficial microalloying elements. Under this guidance, a series of beneficial microalloying elements could be quickly discovered. This
method will help quickly choose beneficial microalloying elements for enhancing GFA and build a foundation for further quantitative analysis of minor alloying.

**Acknowledgments**

This work was supported by The Fundamental Research Funds for the Central Universities (Grant No. 170708019).

**ORCID iDs**

DeChuan Yu © https://orcid.org/0000-0003-3861-1299

**References**

[1] Inoue A and Takeuchi A 2011 Recent development and application products of bulk glassy alloys Acta Mater. 59 2243–67
[2] Wang W H 2007 Roles of minor additions in formation and properties of bulk metallic glasses Prog. Mater. Sci. 52 540–96
[3] Lu Z P and Liu C T 2004 Role of minor alloying additions in formation of bulk metallic glasses: a review Mater. Sci. 39 3965–74
[4] Louguine-Luzgin D V, Xie G Q, Zhang Q S and Inoue A 2010 Effect of Fe on the glass-forming ability, structure and devitrification behavior of Zr–Cu–Al bulk glass-forming alloys Philos. Mag. 90 1955–68
[5] Baulin O, Douillard T, Fabregue D, Perez M, Pelletier J-M and Bugnet M 2019 Three-dimensional structure and formation mechanisms of Y2O3, hollow-precipitates in a Cu-based metallic glass Mater. Des. 168 107660–7
[6] 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
[7] Wang W H, Ru J W, Fan G J and Eckert J 2001 Formation and properties of Zr–(Ti, Nb)–Cu–Ni–Al bulk metallic glasses Mater. Trans. 42 587–91
[8] Wang W H and Bai H Y 2000 Carbon-addition-induced bulk ZrTiCuNiBe amorphous matrix composite containing ZrC particles Mater. Lett. 44 59–63
[9] Kato H and Inoue A 1997 Synthesis and mechanical properties of bulk amorphous Zr–Al–Ni–Cu alloys containing ZrC particles Mater. Trans., JIM 38 793–800
[10] Lu Z, Shen J, Xing D, Sun J and Liu C 2006 Binary eutectic clusters and glass formation in ideal glass-forming liquids Appl. Phys. Lett. 89 071910–3
[11] Li P, Wang G, Ding D and Shen J 2014 Glass forming ability, thermodynamics and mechanical properties of novel Ti–Cu–Ni–Zr–Hf bulk metallic glasses Mater. Des. 53 145–51
[12] Li P 2016 Effect of the Cu and Ni content on the crystallization temperature and crystallization mechanism of La–Al–Cu(Ni) metallic glasses AIP Adv. 6 025010–6
[13] Miracle D B 2004 Efficient local packing in metallic glasses J. Non-Cryst. Solids 342 89–96
[14] 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–Fe–Cu system Mater. Lett. 157 299–302
[15] 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
[16] Yu D C, Li X, Wu Y L and Li S L 2019 Understanding and designing good glass formers in Zr–Al–Co–(Nb) system combining clusters and mixing entropy Mater. Lett. 234 291–3
[17] Yu D, Qiu 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 2021
[18] Makino A, Kubota T, Chang C, Makabe M and Inoue A 2007 FeSiBP bulk metallic glasses with unusual combination of high magnetization and high glass-forming ability Mater. Trans. 48 3624–7
[19] Li X, Qin C L, Kato H, Makino A and Inoue A 2011 Mo microalloying effect on the glass-forming ability, magnetic, mechanical and corrosion properties of (Fe0.76Si0.096B0.084P0.06)100−x(Mo)x bulk glassy alloys J. Alloy. Compd. 509 7688–91
[20] Wang Q, Zhu C L, Li Y H, Cheng X, Chen W R, Wu J, Qiang J B, Wang Y M and Dong C 2008 Co- and Fe-based multicomponent bulk metallic glasses designed by cluster line and minor alloying J. Mater. Res. 23 1543–50
[21] Naz G J, Dong D, Geng Y, Wang Y and Dong C 2017 Composition formulas of Fe-based transition metals-metalloid bulk metallic glasses derived from dual-cluster model of binary eutectics Sci. Rep. 7 9150–60
[22] Gaskell P H 1978 A new structural model for transition metal–metalloid glasses Nature 276 484–5
[23] Miracle D B, Sanders W S and Senkov O N 2003 The influence of efficient atomic packing on the constitution of metallic glasses Philos. Mag. 83 2409–28