Journal of Alloys and Compounds 646 (2015) 620–625

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

A new method locating good glass-forming compositions

Dechuan Yu [a, b], Yan Geng [a], Zhengkun Li [b], Dingming Liu [a, b], Huameng Fu [b], Zhengwang Zhu [b], Yang Qi [a, *], Haifeng Zhang [b, *]

[a] Department of Materials Physics and Chemistry, Northeastern University, No.3-11, Wenhua Road, Shenyang, 110819, PR China
[b] Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang, 110016, PR China

ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form
27 May 2015
Accepted 28 May 2015
Available online 18 June 2015

Keywords:
Amorphous materials
Rapid-solidification
Metallic glasses
Clusters

ABSTRACT

A new method was proposed to pinpoint the compositions with good glass forming ability (GFA) by combining atomic clusters and mixing entropy. The clusters were confirmed by analyzing competing crystalline phases. The method was applied to the Zr–Al–Ni–Cu–Ag alloy system. A series of glass formers with diameter up to 20 mm were quickly detected in this system. The good glass formers were located only after trying 5 compositions around the calculated composition. The method was also effective in other multi-component systems. This method might provide a new way to understand glass formation and to quickly pinpoint compositions with high GFA.

1. Introduction

Increasing attention has been paid to bulk metallic glasses (BMGs) which are expected to be structural and functional materials [1,2]. As far as metallic glasses are concerned, the glass-forming ability (GFA) is one key point for application [3]. In order to expand their application scope, in the past decade, lots of work and theories were reported on the GFA. On this score, early theories, such as confusion principle, Inoue's three empirical rules and deep eutectics, laid an important foundation for understanding glass formation [4–6]. However, for the particular aspect of designing BMG compositions, it still costs time and money under their guidelines.

Recently, a series of novel methods have been raised to design BMG compositions [7–18]. According to methods' physical principles and math representation, these methods can be generally divided into two types: model methods and thermodynamics methods. (1) Model methods. Topologically efficient cluster-packing model and cluster-plus-glue atom model were raised to understand glass formation [7,12–16]. The key point of model methods is to treat the clusters as the basic units of glass; (2) Thermodynamics methods. For instance, the mixing enthalpy was used to design BMG compositions. This method has been successfully applied to design Zr–Al–Fe–Cu and Zr–Al–Ni–Cu glass formers [9,10].

Among the BMGs, Zr-based amorphous alloys attract a great deal of attention owing to the high strength, high corrosion resistance and good biocompatibility [10,19–22]. A series of alloy systems such as Zr–Al–TM (here TM = Fe, Co, Ni, Cu), Zr–Al–Cu–TM (here TM = Ni, Fe) and Zr–Al–TM–Ag (here TM = Ni, Co, Cu) are developed in Zr-based alloy system [1,9,10,20,21,23–25]. It is proved that BMGs with larger GFA usually are obtained in complex system more easily than that in simple system [19]. Unfortunately, with the guidance of upon composition design methods, it is still quite difficult to search good glass-forming composition in the complex alloy system with quinary elements such as Zr–Al–Ni–Cu–Ag. It is expected to quickly pinpoint the compositions with high GFA after limited try.

In this paper, a new method was proposed, combining the atomic clusters and mixing entropy, to understand glass formation and design good glass formers in multicomponent system. Actually, it is worth noting that, different from the above methods, this new method combines the model method and thermodynamics method to design BMG compositions. As an example, some existing typical BMG compositions were analyzed with the use of this new method. Moreover, glass formers with high glass forming ability in a multicomponent system Zr–Al–Ni–Cu–Ag were also identified.

* Corresponding authors.
E-mail addresses: qiyang@imp.neu.edu.cn (Y. Qi), hfzhang@imr.ac.cn (H. Zhang).

http://dx.doi.org/10.1016/j.jallcom.2015.05.184
0925-8388/

2. Composition design

The forming of amorphous alloy experienced the competing process of disordering and ordering phases. During the solidification, the constituent elements with large negative mixing enthalpy usually tend to form short-range order clusters. The great amount of clusters will retard the atomic mobility and redistribution, finally avoid the precipitation of crystalline phases. The clusters will survive until the solidification finishes. It has been recognized that metallic glass can be regarded as a mixture of different clusters. In this paper, we analyze the possible clusters using mixing enthalpy.

Based on the above discussion, in a ternary glassy system of A–B–C, the good glass former C_{am}, on condition that the heat of mixing for each atomic pair is negative, can be regarded as the sum of cluster A–B, cluster A–C and cluster B–C, which can be obtained as follows: $C_{am} = \alpha$ [cluster(A–B)]+β [cluster(A–C)]+ γ [cluster(B–C)], where α, β and γ are coefficients.

It has been reported that the local structures of clusters in amorphous alloys are similar to those in the competing crystalline phases [11,26]. In this paper, the cluster is derived from a local structure by analyzing the crystalline phases. In this case, the ideal composition of good glass former C_{am} is determined by the ratio between α and β along with the ratio between α and γ.

Entropy of mixing plays an important role in glass formation. A series of new high entropy BMGs were found from the existing BMGs with high GFA from the view of mixing entropy [17,18]. For those complex glassy systems with high-order component, it would be more difficult for each atom to quickly rearrange its position to satisfy the need of the requirements of forming crystalline phases upon cooling. That is to say, high mixing entropy is beneficial to glass formation. In this work, the coefficients of the two ratios would be taken at the critical point that achieves the maximum of mixing entropy with the expectation of reaching the largest extent of system's chaos to curb the trend of forming competing crystalline phases.

As mentioned above, the ideal glass is regarded as a mixture of different clusters which are derived from the possible competing crystalline phases by comparing the heat of mixing. The final ideal composition C_{am} is determined by the ratio between different clusters obtained by the calculation of entropy of mixing. By treating different kinds of clusters as the basic units of metallic glass, under the limiting condition of the calculation of entropy of mixing, a new method to understand glass formation and to design BMG compositions was raised.

In the system of Zr–Al–Ni–Cu–Ag, Ni and Ag atoms are expected to occupy the same sites of Cu in the cluster formula as Ni and Ag are the similar elements of Cu. Along with the idea, we first simplify the complex system Zr–Al–Ni–Cu–Ag to a pseudo ternary system Zr–Al–Cu (Ni, Ag), where the enthalpies of mixing of the atomic pairs Zr–Cu, Zr–Al, and Cu–Al at equi-atomic compositions are −23 kJ/mol, −44 kJ/mol and −1 kJ/mol, respectively [27]. It can be seen that the heat of mixing of atomic pairs Zr–Cu and Zr–Al are more negative than that of Cu–Al pair, so that separate Zr–Cu and Zr–Al atomic clusters are more favored than Al–Cu cluster in the Zr–Al–Cu ternary system.

In the present work, Al–Zr binary clusters are derived from Zr-riched eutectic phases in Al–Zr phase system, including AlZr (BCr type), $AlZr_2$ ($InNi_2$ type), $AlZr_2$ (Al_2Cu type), $AlZr_3$ ($AuCu_3$ type), Al_2Zr_3 (Al_2Zr_3 type), Al_3Zr_5 (Mn_5Si_3 type) and Al_3Zr_5 (Si_3W_5 type) as well, from which two clusters centered by small atom Al, namely, one Archimedean octahedral anti-prism CN_8 Zr_8Al_3 cluster derived from phase $AlZr_2$ (Al_2Cu type) and a capped trigonal prism cluster CN_9 Zr_9Al_3 derived from phase Al_3Zr_5 (Mn_5Si_3 type), are obtained (CN signifies the number of atoms in the 1st coordination shell of cluster). The results are consistent with the results reported by Dong et al. [7]. The clusters Zr_8Al_3 and Zr_9Al_3 are shown in Fig. 1.

Between the two clusters, Archimedean octahedral anti-prism CN8 Zr_8Al_3 cluster belongs to one of several fundamental polyhedrons, called Bernal Polyhedrons, proposed by Bernal, to build blocks of amorphous alloys [28]. Except the fundamental types of building amorphous alloys, the degree of efficient packing in cluster is also of great importance. The ideal critical radius ratio R* that achieves most efficient local packing in clusters is calculated in terms of CN [12]. △is defined as the percent difference between the actual radio $R_{0/1}$ and the ideal R* radio. The actual ratios of the cluster $R_{0/1}$ in cluster Al–Al_2Zr_8 is 0.913, where the Goldschmidt radius of Zr, Al used in this calculation are 0.160 and 0.143 nm. R* is 0.799 in clusters Al–Al_2Zr_8 as the CN of cluster Al–Al_2Zr_8 is 10. Δ in cluster Al–Al_2Zr_8 is 14.3%. It can be seen cluster Al–Al_2Zr_8 is close to the requirement of topological close-packing. Furthermore, clusters with CN = 11are not expected to be observed in metallic glasses [12]. For all of the above reasons, in this paper, cluster Zr_8Al_3 with CN = 10 is selected as the basic cluster for Al–Zr binary cluster.

Similar to the case discussed above, a Cu-centered Cu_8Zr_5 cluster is adopted as the Cu–Zr binary cluster, due to the fact that Cu_8Zr_5 is efficiently topological packed and its existence in Cu–Zr amorphous alloys has been proven by previous study [7,16].

As discussed above, the good glass former C_{BMG} in this pseudo ternary system Zr–Al–Cu can be obtained as:

$$C_{BMG} = \alpha[\text{cluster}(Cu{-}Cu_7Zr_5)] + \beta[\text{cluster}(Al - Al_2Zr_8)] \quad (1)$$

For a certain glass former C_{BMG}, its composition depends on φ which stands for the ratio between β and α. As mentioned above, the value of φ would be determined by mixing entropy. Under the consideration of the effect of atomic size mismatch, the mixing entropy of regular liquids can be expressed as [29,30]:

$$\Delta S^{mix} = -R\sum_{i=1}^{n} C_i \ln \Phi_i \quad (2)$$

$$\Phi_i = \frac{c_i r_i^3}{\sum_{i=1}^{n} c_i r_i^3} \quad (3)$$

where R is the gas constant, Φ_i is the atomic volume fraction of the ith component and r_i is the atomic radius.

It is clear that there is a function relationship between the mixing entropy of glass former and the ratio φ (φ = α/β). The glass former is expected to describe the basic feature of amorphous structure, to have strong local order satisfying the topological close-packing requirement from the aspect of microstructure. In addition, the final composition is expected to curb the trend of forming competing crystalline phases by its high mixing entropy from the

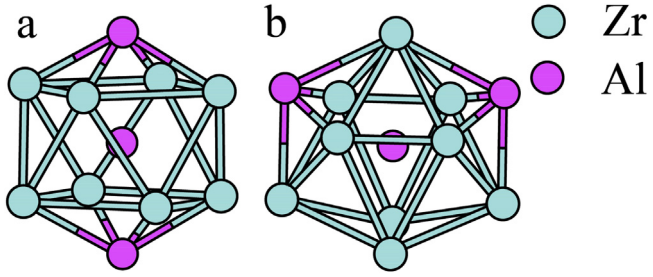

Fig. 1. Images of clusters (a: Cluster Zr_8Al_3 derived from phase $AlZr_2$, b: Cluster Zr_9Al_3 derived from phase Al_3Zr_5).