HOSTED BY

ELSEVIER

CrossMark

Available online at www.sciencedirect.com

ScienceDirect

Progress in Natural Science: Materials International 24 (2014) 350–353

Progress in Natural Science Materials International

www.elsevier.com/locate/pnsmi
www.sciencedirect.com

Original Research

Glass forming ability of Zr–Al–Ni(Co,Cu) understood via cluster sharing model

Jixiang Chen*, Yi Cheng

Department of Physics, Dalian Maritime University, Dalian 116026, China

Received 14 October 2013; accepted 20 May 2014
Available online 22 July 2014

Abstract

Clusters are shared atoms in different ways with their neighboring clusters in the crystalline phases. Cluster formula [effective cluster]$_1$(glue atom)$_x$ can be used to describe crystalline phases, and the effective cluster means the true cluster composition due to cluster overlapping in the phase structure. Degree of cluster sharing of Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) phases is investigated in this paper. Ni_3Zr_9, Co_3Zr_8 and Cu_5Zr_{10} clusters are highlighted because they have the least degree of sharing and can best represent the local atomic short-range order features of the formed phases. It is pointed out that the least sharing clusters are correlated with metallic glass formation and are verified by experiments.

Keywords: Cluster; Cluster formula; Cluster sharing model; Glass forming ability

1. Introduction

In both crystalline and non-crystalline alloys, dissimilar atoms tend to form first-shell coordination polyhedra, called clusters for simplicity, and these clusters constitute the characteristic local atomic features of the formed phases [1,2]. However, the cluster information is usually submerged in the structure describing for quasicrystals, metallic glasses and alloy phases. This is why the compositions are in general unrelated to their structure features.

In our previous works, "cluser-plus-glum-atom" model has been developed for quasicrystals, metallic glasses and alloy phases [3–8]. The key point lies in the dissociation of any structure into two parts, a cluster part and a glue atom part, expressed by cluster formula as [cluster]$_1$(glue atom)$_x$. It is revealed by our previous works that the clusters are shared atoms with their neighboring clusters in alloy phases and the effective clusters have to be used to define the relevant alloy phases [7,8]. In contrary, for metallic glasses and quasicrystals, sharing is not required and the cluster formulas contain the original isolated clusters [6].

Then the most prominent difference in the cluster formulas for crystalline and non-crystalline phases seems to lie in the ways cluster are shared. For this objective, the present paper investigates the cluster configurations of Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) alloy phases, because they are primary devitrification phases of Zr-based bulk metallic glasses (BMGs) of Zr–Al–Ni, Zr–Al–Co and Zr–Al–Cu systems [9–11], respectively. It will be shown that indeed there is a least-shared cluster in an alloy phase that has close relationships with metallic glass formation.

2. Cluster sharing model

In previous works we utilized the cluster formula [effective cluster](glue atoms)$_x$ to express alloy phases [7,8]. Effective clusters are introduced because clusters are usually shared atoms with their neighboring clusters so that their true compositions are different from those of the isolated clusters.

*Corresponding author. Tel.: +86 411 8472 5276.
E-mail address: chenjx@dl.cn (J. Chen).
Peer review under responsibility of Chinese Materials Research Society.

http://dx.doi.org/10.1016/j.pnsc.2014.06.007
1002-0071/

The least cluster sharing means mostly pronounced cluster features, so it should best represent the local atomic short-range order of the phase structure [12]. The number ratio of atoms in the isolated cluster over that in the effective cluster can be used to assess quantitatively the degree of cluster sharing. Following, Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) alloy phases are taken as examples to illustrate the cluster sharing model.

2.1. Zr_6Al_2Ni ($InMg_2$), space group $p\bar{6}2m$, $a=0.7920$ nm, $c=0.3340$ nm

There are four non-equivalent atomic sites in this hexagonal phase, as shown in Table 1 (the structure data used in this paper are all taken from reference [13]). The relevant clusters [14,15] are Ni(0,0,1/2)-centered CN11-Ni_3Zr_9 (coordination number 11, CN=11), Al(1/3,2/3,0)-centered CN11-Al_3Zr_9, Zr (1/4,0,0)-centered CN14-$Zr_{11}Al_2Ni_2$ and Zr(0.59,0,1/2)-centered CN13-Zr_9Al_4Ni (Hereafter, the first element in a cluster expression represents the central atom in the cluster, the subscript number denotes the number of atoms). None of these clusters exists in isolation from its neighboring clusters, as can be easily seen from Fig. 1(b). Extensive overlaps due to sharing of atoms of neighboring clusters deduce the initial clusters to effective ones. For instance the Ni(0,0,1/2)-centered capped trigonal prism Ni_3Zr_9 has its three Ni(0,0,1/2) atoms triple-shared, six Zr(1/4,0,0) atoms double-shared and three Zr (0.59,0,1/2) atoms unshared. So after sharing, the effective one is $NiZr_6$ and what remain outside the cluster part are two Al glue atoms (Fig. 1(a)). Following the scheme of the cluster-plus-glue-atom model, the phase composition and structure can be described with cluster formula $Zr_6Al_2Ni=[NiZr_6]Al_2$. Therefore the degree of sharing of this cluster is $12/7=1.71$. Similarly, the Al(1/3,2/3,0)-centered CN11-Al_3Zr_9 has its three Al(1/3,2/3,0) atoms triple-shared, three Zr(1/4,0,0) atoms double-shared and the other six Zr(0.59,0,1/2) atoms quadruple-shared. So the initial cluster is reduced to $AlZr_3$ after sharing. Zr(1/4,0,0)-centered CN14-$Zr_{11}Al_2Ni_2$ has its two Al(1/3,2/3,0) atoms triple-shared, two Ni(0,0,1/2) atoms sixfold-shared, five Zr(1/4,0,0) atoms fivefold-shared and the other six Zr(0.59,0,1/2) atoms sixfold-shared, and the effective one is $Zr_2Al_{2/3}Ni_{1/3}$. Zr(0.59,0,1/2)-centered CN13-Zr_9Al_4Ni has its four Al(1/3,2/3,0) atoms sixfold-shared, one Ni(0,0,1/2) atoms triple-shared, six Zr(1/4,0,0) atoms sixfold-shared and the other three Zr(0.59,0,1/2) atoms triple-shared, and the effective one is $Zr_2Al_{2/3}Ni_{1/3}$. So after sharing Al_3Zr_9, $Zr_{11}Al_2Ni_2$ and Zr_9Al_4Ni initial clusters are reduced to $AlZr_3$, $Zr_2Al_{2/3}Ni_{1/3}$ and $Zr_2Al_{2/3}Ni_{1/3}$. The degrees of sharing of

Table 1
Structure and cluster data of Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) phases[13].

Phase and type	Size of unit cell (nm)			Atom type	Atomic positions			Isolated clusters	Effective clusters	Degree of sharing
	a	*b*	*c*		*x*	*y*	*z*			
Zr_6Al_2Ni ($InMg_2$)	0.7920	0.7920	0.3340	Ni	0	0	1/2	Ni_3Zr_9	$NiZr_6$	1.71
				Al	1/3	2/3	0	Al_3Zr_9	$AlZr_3$	3.00
				Zr	0.25	0	0	$Zr_{11}Al_2Ni_2$	$Zr_2Al_{2/3}Ni_{1/3}$	5.00
				Zr	0.59	0	1/2	Zr_9Al_4Ni	$Zr_2Al_{2/3}Ni_{1/3}$	4.67
Zr_2Co (Al_2Cu)	0.6363	0.6363	0.5469	Co	0	0	1/4	Co_3Zr_8	$CoZr_2$	3.67
				Zr	0.1679	0.6679	0	$Zr_{12}Co_4$	$ZrCo_{1/2}$	10.67
Zr_2Cu ($MoSi_2$)	0.3220	0.3220	1.1183	Cu	0	0	0	Cu_5Zr_{10}	$CuZr_2$	5.00
				Zr	0	0	0.34	$Zr_{10}Cu_5$	$ZrCu_{1/2}$	10.00

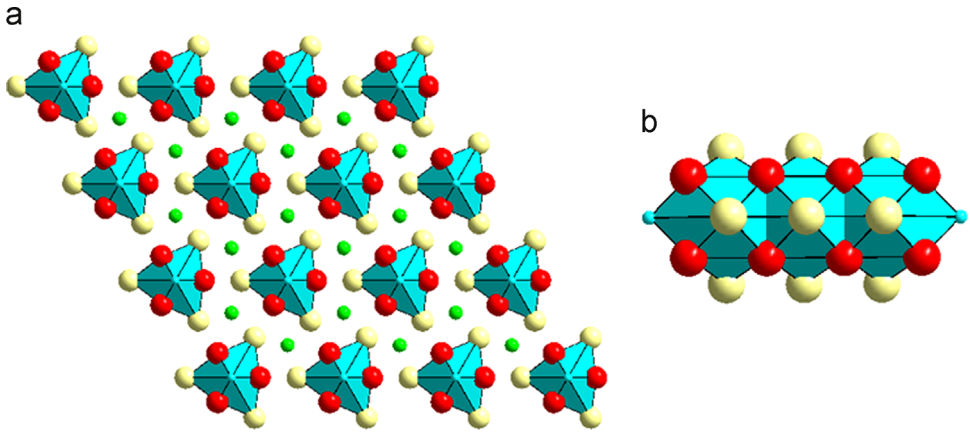

Fig. 1. Zr_6Al_2Ni ($InMg_2$) phase structure analyzed using cluster centered by Ni. The structures are projected along the *c* axis (a) and *a* axis (b).

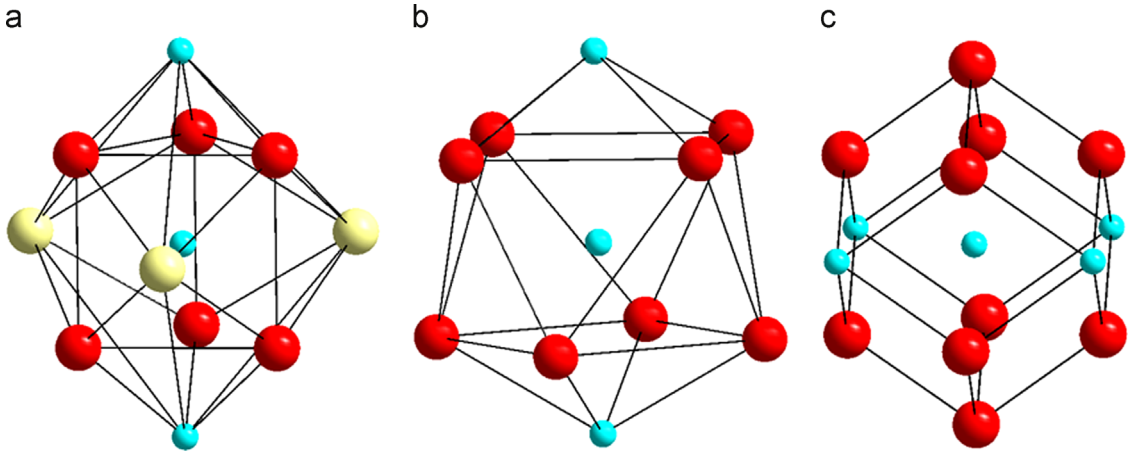

Fig. 2. Configurations of capped trigonal prism CN11-Ni_3Zr_9 from Al_2NiZr_6 ($InMg_2$) phase (a), octahedral antiprism CN10-Co_3Zr_8 from Zr_2Co (Al_2Cu) phase (b), and rhombic dodecahedron CN14-Cu_5Zr_{10} from Zr_2Cu ($MoSi_2$) phase (c). Small spheres represent Ni, Cu, Co atoms and large sphere Zr.

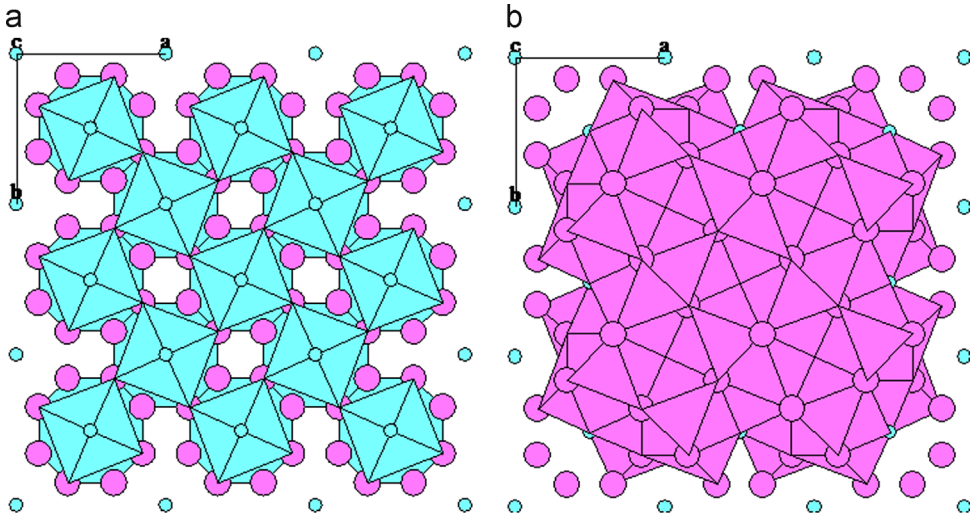

Fig. 3. Zr_2Co (Al_2Cu) phase structure analyzed using clusters centered by two-equivalent atomic sites, Co (a) and Zr (b). The structures are all projected along the *c* axis.

these three clusters are 12/4=3.00, 15/3=5.00 and 14/3=4.67, respectively (shown in Table 1). So Ni_3Zr_9 cluster (Fig. 2 (a)) can be identified the feature of local short-range order for Zr_6Al_2Ni ($InMg_2$) phase because of minimum sharing. Here, notice that the least cluster sharing often leads to cluster formulas with glue atoms so cluster overlaps are not severely.

2.2. Zr_2Co (Al_2Cu), space group I4/mcm, a=0.6363 nm, c=0.5469 nm

This phase contains two non-equivalent atomic occupations in the unit cell. The relevant clusters are CN10-Co_3Zr_8 and CN15-$Zr_{12}Co_4$. After sharing, the effective clusters become $CoZr_2$ and $ZrCo_{1/2}$, and the degrees of sharing are 11/3=3.67 and 16/1.5=10.67. Fig. 3 shows clearly that $Zr_{12}Co_4$ overlaps more severely than Co_3Zr_8. Because of minimum sharing, octahedral antiprism Co_3Zr_8 cluster (Fig. 2(b)) dominates the local atomic short-range order features of Zr_2Co (Al_2Cu) phase.

2.3. Zr_2Cu ($MoSi_2$), space group I4/mmm, a=0.3220 nm, c=1.1183 nm

This simple phase contains two non-equivalent atomic occupations in the unit cell. The relevant clusters are all rhombic dodecahedron CN14-Cu_5Zr_{10}. After sharing, the effective clusters become $CuZr_2$ and $ZrCu_{1/2}$, and the degrees of sharing are 15/3=5.00 and 15/1.5=10.00, as shown in Table 1. So Cu_5Zr_{10} cluster (Fig. 2(c)) best represents the short-range order of the phase structure of Zr_2Cu ($MoSi_2$).

3. From cluster sharing model to bulk metallic glass formation

Recently, 'cluster-plus-glue-atom' structural model has been proposed in order to design BMGs. And it has already been pointed out that BMGs are described only with isolated clusters, satisfying general cluster formula [isolated cluster](glue atoms)$_{1\ or\ 3}$[16–18]. So selecting appropriate clusters is

the key issue to employ cluster-plus-glue-atom model. It would be interesting to link the cluster property of an alloy phase to metallic glass formation. Clusters having the least sharing in the crystalline phases tend to be more isolated, it is then anticipated that BMGs might be related to some of these clusters. According to above analyses and Table 1, Ni_3Zr_9, Co_3Zr_8 and Cu_5Zr_{10} clusters have the least sharing degree in Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) phases, therefore might have close relationship with BMGs.

Zr–Al–Ni is a ternary alloy system having high glass forming abilities [9]. According to our recent work [19,20], $Zr_{60}Al_{13.3}Ni_{26.7}$ composition has the highest glass forming ability. It can be explained by $Zr_{60}Al_{13.3}Ni_{26.7}=[Ni_3Zr_9](NiAl_2)$, where Ni_3Zr_9 is the least sharing cluster of a devitrification phase Zr_6Al_2Ni ($InMg_2$).

It has been reported that the best composition of BMG for Zr–Al–Co system is $Zr_{57}Al_{15}Co_{28}$ [10]. It can be explained by $Zr_{57}Al_{15}Co_{28}=[Co_3Zr_8](CoAl_2)$, where Co_3Zr_8 is the least sharing cluster of Zr_2Co (Al_2Cu) phase.

For Zr–Al–Cu system, the best composition of BMG is $Zr_{65}Al_{7.5}Cu_{27.5}$ [11]. It can be expressed by $Zr_{65}Al_{7.5}Cu_{27.5}=[Cu_5Zr_{10}](Zr_{1.7}Al_{1.3})$, where Cu–centered Cu_5Zr_{10} is the least sharing cluster of Zr_2Cu ($MoSi_2$) phase.

Further work is under way to reveal more interesting things about the properties of clusters and their application in designing alloy composition.

4. Conclusions

1) Clusters are overlapped and shared atoms with their neighboring clusters in crystalline phases.
2) Clusters sharing model of Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) phases reveal that Ni_3Zr_9, Co_3Zr_8 and Cu_5Zr_{10} clusters have the least sharing degree in Zr_6Al_2Ni ($InMg_2$), Zr_2Co (Al_2Cu) and Zr_2Cu ($MoSi_2$) phases.
3) The best compositions of BMGs for Zr–Al–Ni, Zr–Al–Co and Zr–Al–Cu systems was reported as $Zr_{60}Al_{13.3}Ni_{26.7}$, $Zr_{57}Al_{15}Co_{28}$ and $Zr_{65}Al_{7.5}Cu_{27.5}$, and can be explained using cluster formulas as: $Zr_{60}Al_{13.3}Ni_{26.7}=[Ni_3Zr_9](NiAl_2)$, $Zr_{57}Al_{15}Co_{28}=[Co_3Zr_8](CoAl_2)$ and $Zr_{65}Al_{7.5}Cu_{27.5}=[Cu_5Zr_{10}](Zr_{1.7}Al_{1.3})$.
4) The least sharing clusters are related to bulk metallic glasses formation.

Acknowledgments

This work is supported by the Fundamental Research Funds for the Central Universities of China (Grant no.3132014327).

References

[1] A.L. Mackay, J.L. Finney, J. Appl. Crystallog. 6 (1973) 284–289.
[2] R. Wang, Nature 278 (1979) 700–703.
[3] C. Dong, J.B. Qiang, Y.M. Wang, N. Jiang, J. Wu, P. Thiel, Philos. Mag. 86 (2006) 263–274.
[4] C. Dong, Q. Wang, J.B. Qiang, Y.M. Wang, N. Jiang, G. Han, Y.H. Li, J. Wu, J.H. Xia, J. Phys. D: Appl. Phys. 40 (2007) 273–291.
[5] Q. Wang, C. Dong, J.B. Qiang., Mater. Sci. Eng. A 18 (2007) 449–451.
[6] J.H. Xia, J.B. Qiang, Y.M. Wang, Q. Wang, C. Dong, Appl. Phys. Lett. 88 (2006) 101907.
[7] J.X. Chen, C. Dong, Q. Wang, Chem. Phys. Lett. 502 (2011) 176–179.
[8] J.X. Chen, Q. Wang, Y.M. Wang, J.B. Qiang, C. Dong, Philos. Mag. Lett. 90 (2010) 683–688.
[9] A. Inoue, T. Zhang, T. Masumoto., Mater. Trans. JIM 31 (1990) 177–183.
[10] T. Wada, F.X. Qin, X.M. Wang, M. Yoshimura, A. Inoue, J. Mater. Res. 24 (2009) 2941–2948.
[11] J. Saida, M. Matsushita, K. Yaoita, A. Inoue, Mater. Trans. JIM 40 (1999) 1117–1122.
[12] J.X. Chen, Q. Wang, Y.M. Wang, J.B. Qiang, F.W. Li, C.L. Zhu, C. Dong, Philos. Mag. 92 (2012) 4300–4319.
[13] P. Villars, L.D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases. Desk edition, 1, ASM International, 1997.
[14] J.X. Chen, J.B. Qiang, Q. Wang, C. Dong, Acta Phys. Sin. 61 (2012) 046102 (1–9).
[15] L.J. Luo, J. Wu, Q. Wang, Y.M. Wang, G. Han, C. Dong, Philos. Mag. 90 (2010) 3961–3973.
[16] G. Han, J.B. Qiang, F.W. Li, L. Yuan, S.G. Quan, Q. Wang, Y.M. Wang, C. Dong, P. Häussler, Acta Materialia 59 (2011) 5917–5923.
[17] C.L. Zhu, Q. Wang, Y.M. Wang, J.B. Qiang, C. Dong, J. Alloys Compds. 504S (2010) S34–S37.
[18] C.L. Zhu, Q. Wang, Y.J. Zhao, Y.M. Wang, J.B. Qiang, C. Dong, Sci. Chin. Ser. G: Phys., Mech. Astron. 53 (2010) 440–444.
[19] Y.H. Li, W. Zhang, C. Dong, J.B. Qiang, A. Makino, A. Inoue, Intermetallics 18 (2010) 1851–1855.
[20] F.W. Li, J.B. Qiang, Y.M. Wang, Q. Wang, X.L. Dong, C. Dong, Chin. Sci. Bull. 56 (2011) 3902–3907.