Preferred clusters in metallic glasses*

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In this work, we present a feasible scheme based on framework of the sophisticated Voronoi tessellation method in order to evaluate what clusters should be preferred for building blocks in any given metallic glass, by analysing the fivefold-symmetry axes as well as the degree of structural regularity in various clusters. This scheme is well proved by a group of experiments and calculations, which may have broad implications for exploration of obtaining explicit and proper structural pictures, and understanding the structural origin of the unique properties and glass forming ability in these novel amorphous alloys.

Keywords: metallic glass, synchrotron radiation techniques, atomic structure, reverse Monte Carlo simulation

PACC: 6110, 6155H, 7870D, 4170

1. Introduction

The atomic structure of metallic glasses (MGs) is a long-standing issue, which has been largely investigated by scientists,[1−8] but hitherto remains unresolved due to its intrinsic complexity. Although MGs lack the long-range ordering caused by stacking unit cells periodically in various crystalline alloys, angstrom-scale atomic clusters have been recognized as their structural building blocks.[1] The configuration and the spatial connection of these building blocks may contribute to topological and chemical ordering at short or even medium range.[2−4] However, unlike the fact that SiO_4 tetrahedra are known as the basic structural units in silicate glasses, efforts have failed to find out certain determined clusters that could be the predominant building block in all MG compositions. For instance, although icosahedral cluster (with one centre and 12 shell atoms) has been reported to be the dominant structural unit in many MGs,[9−11] it could not be extended to all MG compositions because of the following analysis. First, according to Miracle's solute-centred cluster model,[2] the number of solvent (shell) atoms in each cluster, i.e, corresponding coordination number (CN) of the central atom, strongly depends on R^* (the optimal radial ratio of solute/solvent atoms). In fact, in various developed MGs, their atomic radial ratios of solute/solvent may be close to different R^* values, resulting in corresponding preferred clusters with different CNs. Secondly, it has been pointed out that some dominant quasi-equivalent clusters may form the structural backbone of each MG, which can make a moderate CN distribution.[3] However the types of the preferred clusters may change with alloy system and even composition. The above analysis may accordingly raise a question of whether we can find out what angstrom-scale clusters should be preferred in any given MG composition. In this work, we present a feasible scheme based on the framework of sophisticated Voronoi tessellation method in order to evaluate which clusters should be preferred in each MG composition. The scheme is well proved by a group of experiments or calculations.

2. Scheme for selecting preferred clusters

Voronoi tessellation analysis is an effective 3-dimensional (3D) approach to building atomic clusters with one central atom.[1,12] According to Voronoi original algorithm,[13] a convex Voronoi polyhedron (VP)

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can be built by connecting perpendicular bisectors between a central atom and all of its neighbouring atoms, which may be indexed as $\langle n3, n4, n5, n6 \ldots \rangle$, where ni denotes the number of i-edged faces on surface of this polyhedron. Each VP should be embedded in a corresponding convex Voronoi cluster (VC), which is composed of a solute (centre) atom and its neighboured solvent (shell) atoms (configurations of some VCs and corresponding VPs refer to Fig. 1 in this work or Fig. 6 in Ref. [12]). Thus $\sum ni$ also represents the number of the shell atoms in one VC, i.e., CN of the central atom. Voronoi algorithm also requires that all VCs should be closed structural units, which could be built by piling up a set of Delaunay tetrahedrons with the common vertex at an atom (the central atom of VC),[14] resulting in the fact that their surface should be composed only of triangle faces, i.e., they could be regarded as deltahedra.[3] Then take into account Euler's formula

$$V - E + F = 2, \tag{1}$$

where V, E and F denote the numbers of vertexes (occupied by atoms), edges and faces of VCs, respectively. V (CN), F and E here should satisfy the following equations:

$$\begin{aligned} 3E &= 2F = \sum i \times ni, \\ V &= 0.5F + 2. \end{aligned} \tag{2}$$

Obviously, $\sum i \times ni$ must be divisible by 6.

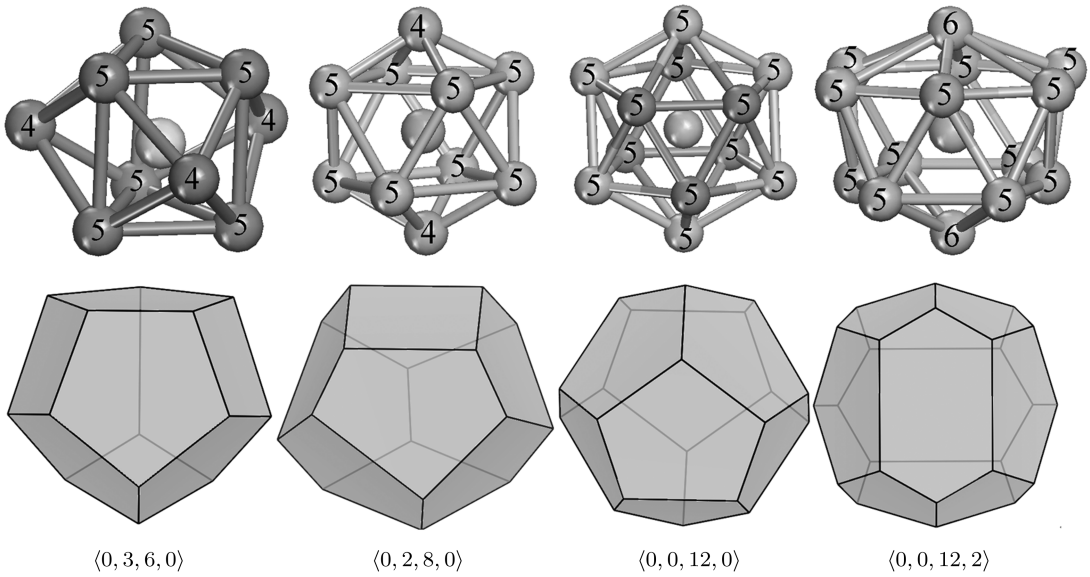


Fig. 1. Topological structures of representative regular VCs (ball and stick) and their corresponding VPs. They could be extracted in atomic structure of some intermetallic compounds. For instance, $\langle 0, 3, 6, 0 \rangle$, $\langle 0, 2, 8, 0 \rangle$, $\langle 0, 0, 12, 0 \rangle$ and $\langle 0, 0, 12, 2 \rangle$ here are extracted from atomic structure of orthogonal Ni_3B_1 phase, tetragonal Zr_5Al_3 phase, cubic Zr_2Ni_1 phase and tetragonal Zr_5Al_3 phase, respectively. The numbers labeled on shell atoms denote these atoms are i-coordinated ones on the shell, and also stand for these shell/central atomic lines are i-fold axes of symmetry.

So far, using Voronoi tessellation approach, a number of indexed VCs have been deduced in various MGs, usually with CN ranged from 8 to 14.[3,12] In the present work, in order to present a scheme for selecting preferred clusters from these VCs, we introduce the concept of axes of symmetry in the convex VCs, which is one essential structural feature. In detail, because each shell-central atomic bond in VC is perpendicular to one corresponding i-edged face of VP, it may be regarded as an i-fold axis of symmetry. Therefore, each VC could be analysed by classifying its symmetry axes. For instance, $\langle 0, 2, 8, 2 \rangle$ denotes a VC possessing 2 fourfold-, 8 fivefold- and 2 sixfold-symmetry axes. In crystallography, it is well known that fivefold-symmetry axis is forbidden in regularly-repeating component of crystal, namely the unit cell.[15] In this sense, VCs with abundant fivefold-symmetry axes may eliminate their possibility of being structural units arranged periodically in crystals. Thus we may propose a simple criterion to select preferred clusters in MGs by counting the number

of their fivefold-symmetry axes. As shown in Table 1, we sort all convex VCs with a CN range of 8–14 according to their priority evaluated by this criterion.

Table 1. The sorted VCs according to their order of priority. Judging by our criterion to count the number of fivefold-symmetry axis, VCs with the same CN are denoted by series numbers of ①, ②, ③ ..., which are usually found by Voronoi tessellation analysis on MGs.

serial numbers	CNs of VCs						
	8	9	10	11	12	13	14
①	$\langle 0,4,4,0\rangle$	$\langle 0,3,6,0\rangle$	$\langle 0,2,8,0\rangle$	$\langle 0,2,8,1\rangle$	$\langle 0,0,12,0\rangle$	$\langle 0,1,10,2\rangle$	$\langle 0,0,12,2\rangle$
②	$\langle 0,6,0,2\rangle$	$\langle 0,4,4,1\rangle$	$\langle 0,3,6,1\rangle$	$\langle 0,3,6,2\rangle$	$\langle 0,2,8,2\rangle$	$\langle 0,2,8,3\rangle$	$\langle 0,1,10,3\rangle$
③		$\langle 0,5,2,2\rangle$	$\langle 0,4,4,2\rangle$	$\langle 0,4,4,3\rangle$	$\langle 0,3,6,3\rangle$	$\langle 0,3,6,4\rangle$	$\langle 0,2,8,4\rangle$
④			$\langle 0,5,2,3\rangle$	$\langle 0,5,2,4\rangle$	$\langle 0,4,4,4\rangle$	$\langle 0,4,4,5\rangle$	$\langle 0,3,6,5\rangle$
⑤					$\langle 0,5,2,5\rangle$	$\langle 0,5,2,6\rangle$	$\langle 0,4,4,6\rangle$
⑥							$\langle 0,5,2,7\rangle$

3. Experiments and simulations

Although we have proposed a scenario on the order of priority of possible VCs in MGs, it should be examined. Fortunately, the synchrotron radiation-based experiments combined with theoretical calculation or simulation have become a state-of-the-art method to diagnose the atomic structures of MGs, which is adopted in the present work to address this issue. In this work, $Zr_{70}Cu_{30}$, $Zr_{55}Cu_{45}$ binary and $Zr_{48}Cu_{45}Al_7$ ternary amorphous ribbons were fabricated from master alloys by single-roller melt spinning in purified Ar atmosphere. Subsequently, room temperature x-ray diffraction (XRD) measurements were performed for all samples with a high-energy synchrotron radiation monochromatic beam (about 100 keV). Diffraction data were collected by a Mar345 image plate. These two-dimensional patterns were integrated to Q-space by using program Fit2D[16] and the output data were normalized by software PDFgetX to obtain structure factor $S(Q)$. In addition, extended x-ray absorption fine structure (EXAFS) measurements for Zr and Cu K-edge were carried out at beamline X1 in Hasylab of Germany by using transmission mode. Measured spectra were analysed via standard procedures of data reduction by using program Viper.[17] Furthermore, reverse Monte Carlo simulation technique[3,12] was utilized. Boxes containing 20000 random packed atoms matching all the selected compositions were built to simulate their $S(Q)$ and EXAFS data synchronously. The corresponding atomic structures were carefully analysed by Voronoi tessellation method and various VCs were extracted. Here we plotted the experimental $S(Q)$ and EXAFS data of $Zr_{55}Cu_{45}$, along with their corresponding simulated spectra in Fig. 2 (the data of $Zr_{55}Cu_{45}$ and $Zr_{48}Cu_{45}Al_7$ are not shown here). It is found that an excellent match is achieved for all data, which may ensure reliability by eliminating the random computational convergence.

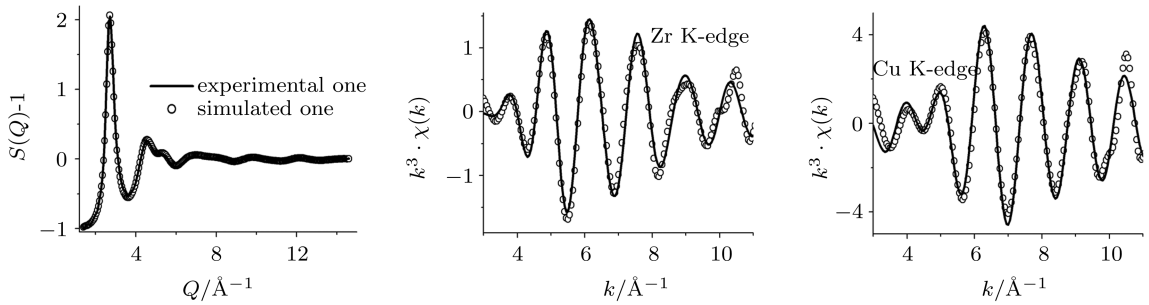


Fig. 2. $S(Q)$, Zr K-edge and Cu K-edge EXAFS experimental (solid lines) and simulated (circles) data (1 Å = 0.1 nm).

4. Results and discussion

In Table 2 we summarize the order of priority of some major VCs according to their weights in a number of MGs, whose atomic structures were investigated in Refs. [3], [18]–[33] as well as the present work. In spite of the inevitable systematic and statistical errors in the experiments and simulations, the priority order of VCs with CN of 8, 9, 11 and 13 sorted in Table 2 matches well with that in Table 1, which indicates that our scheme is successful in selecting preferred clusters in these types of VCs. However, concerning CN-10, –12 and –14 VCs, their priority orders derived from experimental data seem different with those in Table 1: the ①-marked VCs only take the second (the third or even the fourth) place in many MGs in Table 2. This means that these VCs do not take priority over other clusters with the same CN. To explain this phenomenon, some other structural features of these VCs should be analysed.

Table 2. Sorted VCs according to their order of priority obtained from experiments and simulations. The series numbers denote the same VCs in Table 1. Either fraction distribution of VCs was directly provided, or their priority of order was given in these references. Here we choose the solute-centred VCs. We also ignore some VCs in several literatures whose indices are forbidden according to Eq. (2) in Section 2.

metallic glasses	central atom	CNs of major VCs							references
		8	9	10	11	12	13	14	
$Zr_{70}Cu_{30}$	Cu		①②	②①③	①②③	②③④①	①		present work
Zr_2Cu	Cu	①	①	②①③	①③②	②③①			Ref. [18]
$Zr_{55}Cu_{45}$	Cu		①②	②①③	①②③	②③①④	①		present work
$Cu_{50}Zr_{50}$	Cu			①②③	①②③	②①③			Ref. [19]
$Zr_{45}Cu_{45}Ag_{10}$	Cu			①②③	①②③	②①③			Ref. [19]
	Ag			②③	①	②③①	①		Ref. [19]
$Zr_{40}Cu_{40}Ag_{20}$	Cu			①②③	①③②	①②③			Ref. [19]
	Ag			②③	①	②①③	①		Ref. [19]
$Zr_{43}Cu_{57}$	Zr							②③④	Ref. [20]
$Zr_{35}Cu_{65}$	Zr							③④②	Ref. [21]
$Zr_{48}Cu_{45}Al_7$	Cu		①	②①③	①②③	②③①	①		present work
	Al	①	①	①②③	①②③	②			present work
$Zr_{70}Ni_{30}$	Ni			②③①	①③②	②③④			Ref. [22]
$Zr_{66.7}Ni_{33.3}$	Ni	①	①②	②①③	①③②	②③①			Refs. [18] and [23]
$Zr_{50}Ni_{50}$	Ni				①	①②③	①③		Ref. [24]
$Zr_{39}Ni_{61}$	Zr					②③①④	③①②④	②①③④	Ref. [25]
$Zr_{84}Pt_{16}$	–				①	①②③	①③		Ref. [3]
$Zr_{80}Pt_{20}$	Pt		①	②①③	①③②	②③			Ref. [26]
$Zr_{73}Pt_{27}$	Pt				①②③	②③④①			Ref. [27]
$Zr_{70}Pd_{30}$	Pd	①	①②	②①③	①③				Refs. [26] and [28]
$Ni_{81}B_{19}$	–	①	①	①②	①				Ref. [3]
$Ni_{80}P_{20}$	–			①	①	①②			Ref. [3]
$Ni_{50}Mg_{50}$	Ni	①	①②	②①③	①②③	①②③	①		Ref. [29]
$Ni_{40}Pd_{40}P_{20}$	P	①	①	②①③					Ref. [30]
$Ni_{33}Y_{67}$	Ni		①	①②					Ref. [31]
$Fe_{86}B_{14}$	B	①	①②	②①③					Ref. [32]
$Fe_{83}B_{17}$	B	①	①②	②①③	①				Ref. [32]
$Fe_{80}B_{20}$	B	①	①②	②①③					Ref. [32]
$Re_{47}Tb_{53}$	Re					①②③	①②③	②	Ref. [33]
$Re_{11}Tb_{89}$	Re		①	②①	①②③	②			Ref. [33]

We notice that the ①-marked VCs with CN of 10, 12 and 14 ($\langle 0,2,8,0\rangle$, $\langle 0,0,12,0\rangle$ and $\langle 0,0,12,2\rangle$), have a unique structural feature that all the atoms are topo-

logically symmetrically packed on their shells, which indicates that they can be regarded as regular clusters (see Fig. 1). These regular clusters could be constructed manually in atomic structure of some intermetallic compounds.[12,34] Their structural configurations as well as those of corresponding VPs are plotted in Fig. 1. However, concerning other CN-10, –12 and –14 VCs, it is evident that their shell atoms are not symmetrically packed (see Fig. 6 in Ref. [12]), which indicates that they are irregular clusters. We find that these irregular clusters cannot be extracted from atomic structure of any compound phase, which may result from the fact that atoms should be orderly arranged in any direction in crystal phases. Based on the facts above, we suggest that although unlike the unit cells, regular VCs lack translational periodicity, their existence in intermetallic compounds may enhance competitiveness of crystalline phases by facilitating cluster rearrangement during quench. In other words, structural regularity of the VCs contained in crystal alloys may deteriorate their competitiveness as preferred clusters in MGs: the more perfect the regularity, the less the competitiveness is.

Concerning VCs with CN-8, 9, 11 and 13, it is found that all of them are irregular clusters except for $\langle 0,3,6,0\rangle$, which is the ①-marked CN-9 VC and also could be extracted from compound phase. However, unlike other ①-marked VCs ($\langle 0,2,8,0\rangle$, $\langle 0,0,12,0\rangle$ and $\langle 0,0,12,2\rangle$), we notice that $\langle 0,3,6,0\rangle$ always takes the first place in Table 2. Here we explain it by analysis as follows. The first reason may be that the degree of regularity in $\langle 0,3,6,0\rangle$ is less than those of $\langle 0,2,8,0\rangle$, $\langle 0,0,12,0\rangle$ and $\langle 0,0,12,2\rangle$. In crystallography, the degree of regularity strongly depends on the symmetry operation in clusters.[15] Take framework of the $\langle 8,0,0,0\rangle$ VC[12] (the unit cell of body-centred-cubic crystal) for example, it is clear that besides 8 threefold-rotation symmetry axes, all atoms are symmetrically packed on the shell by regarding its centre as a mirror, which indicates that its regularity is extremely high. We notice that in the $\langle 0,0,12,0\rangle$ VC, all the fivefold-coordinated atoms are sited on the shell symmetrically via both rotation and mirror symmetry operations, which indicates that it also possesses high degree of structural regularity. Even for $\langle 0,2,8,0\rangle$ and $\langle 0,0,12,2\rangle$ VCs, some fourfold- or sixfold-coordinated atoms could be symmetrically packed via mirror symmetry operation. However, except for 3 fourfold- and 6 fivefold-rotation symmetry axes, no mirror symmetry feature could be detected in $\langle 0,3,6,0\rangle$, which suggests that it has relatively low degree of structural regularity. The second reason is that the weight of fivefold-symmetry axes is less than 45% in other CN-9 VCs while such a value exceeds 60% in the ②-marked VCs with CN-10, 12 and 14, which indicates that the ②-marked CN-9 VC may have relatively weak competitiveness.

In addition, we can also make a deduction that the priority of ①-marked VCs with CN-10, 12 and 14 may depend on the number of elements in MGs. For instance, by comparing the tabulated results of ZrCu and corresponding ZrCuAg compositions whose major building blocks are VCs with CN-11-12 in Ref. [19], a tendency could be observed that Cu- and Ag-centred $\langle 0,0,12,0\rangle$ VCs become more and more competitive in the queue of CN-12 VCs when Ag is added and their concentration is increased. We explain this phenomenon as follows. By comparison with the ideal icosahedron, it was found that atoms were not strictly orderly packed in $\langle 0,0,12,0\rangle$ in amorphous alloys, which could lead to the geometrical frustration of perfect symmetrical packing with shell atoms and accordingly the deterioration of its structural regularity.[35] It is clear that compared with the case for one binary MG, $\langle 0,0,12,0\rangle$ contains many heterogeneous shell atoms in its corresponding ternary composition, which may lead to more obvious radial mismatch between heterogeneous atoms and enhanced atomic-level chemical fluctuation on the shell. These factors may further aggravate the structural frustration of $\langle 0,0,12,0\rangle$, resulting in its relatively low degree of regularity and enhanced competitiveness as preferred cluster in MGs. Although hitherto the atomic structures of developed multicomponent MGs containing more than 4 elements have rarely been investigated using Voronoi tessellation, we may extrapolatively predict that the regularity of $\langle 0,0,12,0\rangle$ may be more deteriorated in multicomponent MGs with more elements. This analysis may be applicable to other "regular" VCs, such as $\langle 0,2,8,0\rangle$, and $\langle 0,0,12,2\rangle$.

The above scheme may also be used to discuss the atomic structure for a binary system. For instance, it is acknowledged that ZrCu system has a wide composition range where MGs could be fabricated (Cu 30–70 at%). Actually, it is shown in Table 2 that most

clusters with CN range of 8–14 exist in $Zr_{70}Cu_{30}$ or $Zr_{35}Cu_{65}$ and their orders of priority in all VC types are the same. Nevertheless, the large VCs have relatively high fractions in the latter because their VC centres are surrounded with more Cu neighbours (the relatively small atoms).

5. Conclusions

In summary, by analysing the fivefold-symmetry axes as well as the degrees of structural regularity of clusters, a scheme based on Voronoi tessellation analysis, for evaluating preferred VCs in the atomic structures of MGs, is proposed and well validated by a group of experiments and simulations. Although how to provide a visual structural picture of MGs by packing preferred clusters is still a long-standing issue, the present work may provide a feasible scheme for studying atomic structure from cluster perspective, facilitating further understanding of glass forming mechanism of these novel condensed matter systems.

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