Original Research

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

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Abstract

Clusters are shared atoms in different ways with their neighboring clusters in the crystalline phases. Cluster formula [effective cluster](glue atom), 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 Zr6Al2Ni (InMg2), Zr2Co (Al2Cu) and Zr2Cu (MoSi2) phases is investigated in this paper. Ni3Zr9, Co3Zr8 and Cu5Zr10 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.

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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, “cluster-plus-glue-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](glue atom). 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 Zr6Al2Ni (InMg2), Zr2Co (Al2Cu) and Zr2Cu (MoSi2) 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), 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.
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, Zr₆Al₂Ni (InMg₂), Zr₂Co (Al₂Cu) and Zr₂Cu (MoSi₂) alloy phases are taken as examples to illustrate the cluster sharing model.

2.1. Zr₆Al₂Ni (InMg₂), space group p62m, \(a = 0.7920\) 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-Ni₃Zr₉ (coordination number 11, CN=11), Al(1/3,2/3,0)-centered CN11-Al₃Zr₉, Zr (1/4,0,0)-centered CN14-Zr₁₁Al₂Ni₂ and Zr(0.59,0,1/2)-centered CN13-Zr₉Al₂Ni (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 Ni₃Zr₉ 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 NiZr₆ 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 Zr₆Al₂Ni = [NiZr₆]Al₂. Therefore the degree of sharing of this cluster is 12/7 = 1.71. Similarly, the Al(1/3,2/3,0)-centered CN11-Al₃Zr₉ 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 AlZr₃ after sharing. Zr(1/4,0,0)-centered CN14-Zr₁₁Al₂Ni₂ 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 Zr₃Al₂Ni₁/₃. Zr(0.59,0,1/2)-centered CN13-Zr₉Al₂Ni 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 Zr₂Al₂/₃Ni₁/₃. So after sharing Al₂Zr₉, Zr₁₁Al₂Ni₂ and Zr₉Al₂Ni initial clusters are reduced to AlZr₃, Zr₂Al₂/₃Ni₁/₃ and Zr₂Al₂/₃Ni₁/₃. The degrees of sharing of

<table>
<thead>
<tr>
<th>Phase and type</th>
<th>Size of unit cell (nm)</th>
<th>Atom type</th>
<th>Atomic positions</th>
<th>Isolated clusters</th>
<th>Effective clusters</th>
<th>Degree of sharing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr₆Al₂Ni (InMg₂)</td>
<td>0.7920 0.7920 0.3340</td>
<td>Ni</td>
<td>0 0 1/2</td>
<td>Ni₃Zr₉</td>
<td>NiZr₆</td>
<td>1.71</td>
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<td></td>
<td></td>
<td>Al</td>
<td>1/3 2/3 0</td>
<td>Al₃Zr₉</td>
<td>AlZr₃</td>
<td>3.00</td>
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<td></td>
<td></td>
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<td>0.25 0 0</td>
<td>Zₙ₁₁Al₂Ni₃</td>
<td>Zₙ₃Al₂Ni₁/₃</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr</td>
<td>0.59 0 1/2</td>
<td>Zₙ₉Al₂Ni</td>
<td>Zₙ₃Al₂Ni₁/₃</td>
<td>4.67</td>
</tr>
<tr>
<td>Zr₂Co (Al₂Cu)</td>
<td>0.6363 0.6363 0.5469</td>
<td>Co</td>
<td>0 0 1/4</td>
<td>CoZₙ₈</td>
<td>CoZr₂</td>
<td>3.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr</td>
<td>0.1679 0.6679 0</td>
<td>Zₙ₁₂Co₄</td>
<td>Zₙ₁₂Co₁/₂</td>
<td>10.67</td>
</tr>
<tr>
<td>Zr₂Cu (MoSi₂)</td>
<td>0.3220 0.3220 1.1183</td>
<td>Cu</td>
<td>0 0 0</td>
<td>Cu₉Zₙ₁₀</td>
<td>CuZr₂</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr</td>
<td>0 0 0.34</td>
<td>Zₙ₁₀Cu₅</td>
<td>Zₙ₁₀Cu₁/₂</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Fig. 1. Zr₆Al₂Ni (InMg₂) phase structure analyzed using cluster centered by Ni. The structures are projected along the c axis (a) and a axis (b).
these three clusters are $12/4 = 3.00$, $15/3 = 5.00$ and $14/3 = 4.67$, respectively (shown in Table 1). So Ni$_3$Zr$_9$ cluster (Fig. 2(a)) can be identified the feature of local short-range order for Zr$_6$Al$_2$Ni (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$_2$Co (Al$_2$Cu), 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$_3$Zr$_8$ 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$_3$Zr$_8$. Because of minimum sharing, octahedral antiprism Co$_3$Zr$_8$ cluster (Fig. 2(b)) dominates the local atomic short-range order features of Zr$_2$Co (Al$_2$Cu) phase.

2.3. Zr$_2$Cu (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$_5$Zr$_{10}$. 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$_5$Zr$_{10}$ cluster (Fig. 2(c)) best represents the short-range order of the phase structure of Zr$_2$Cu (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
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, Ni3Zr9, Co3Zr8 and Cu5Zr10 clusters have the least sharing degree in Zr6Al2Ni (InMg2), Zr2Co (Al2Cu) and Zr2Cu (MoSi2) 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], Zr60Al13.3Ni26.7 composition has the highest glass forming ability. It can be explained by Zr60Al13.3Ni26.7=[Ni3Zr9](NiAl2), where Ni3Zr9 is the least sharing cluster of a devitrification phase Zr6Al2Ni (InMg2).

The best compositions of BMGs for Zr–Al–Co system is Zr57Al15Co28 [10]. It can be expressed by Zr57Al15Co28=[Co3Zr8](CoAl2), where Co3Zr8 is the least sharing cluster of Zr2Co (Al2Cu) phase.

For Zr–Al–Cu system, the best composition of BMG is Zr65Al7.5Cu27.5 [11]. It can be expressed by Zr65Al7.5Cu27.5=[Cu5Zr10](Zr1.7Al1.3), where Cu5Zr10 is the least sharing cluster of Zr2Cu (MoSi2) 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 Zr60Al13.3Ni26.7, Zr65Al7.5Cu27.5 and Zr65Al7.5Cu27.5 phases reveal that Ni3Zr9, Co3Zr8 and Cu5Zr10 clusters have the least sharing degree in Zr6Al2Ni (InMg2), Zr2Co (Al2Cu) and Zr2Cu (MoSi2) phases.
3) The best compositions of BMGs for Zr–Al–Ni, Zr–Al–Co and Zr–Al–Cu systems were reported as Zr60Al13.3Ni26.7, Zr57Al15Co28 and Zr65Al7.5Cu27.5, and can be explained using cluster formulas as: Zr60Al13.3Ni26.7=[Ni3Zr9](NiAl2), Zr57Al15Co28=[Co3Zr8](CoAl2) and Zr65Al7.5Cu27.5=[Cu5Zr10](Zr1.7Al1.3).
4) The least sharing clusters are related to bulk metallic glasses formation.

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References