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Simulated Cu−Zr Glassy Alloys: the Impact of Composition on Icosahedral Order

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Cu−Zr system is in short list of binary alloys capable to form bulk- metallic glasses (BMG). It has unique glass-forming ability (GFA) where compositions of BMG formation are located in narrow concentration intervals. One of the general ideas explaining this unusual property, strongly supported by molecular dynamics simulations, is the suggestion that local icosahedral order plays important role in GFA. However the definition of local order contains a significant proportion of uncertainty related to the complexity of the definition of the nearest neighbors in disordered media and the difficulty of symmetry-classification of local clusters with non-ideal shape. This problem makes the results of local order analysis rather challenging for practical applications.

In the paper we study structural properties of the simulated $Cu_\alpha Zr_{1-\alpha}$ glassy alloys in the wide range of the copper concentration $\alpha \in (0.2, 1)$ using two different methods to detect the local order: Voronoi tessellation (VT) and Bond Orientational Order Parameters (BOOP). We show that more rigorous BOOP method reveals essentially different results in comparison to those obtained by widely accepted VT method. Comparison of the BOOP and VT demonstrates that the latter significantly overestimates the number of icosahedral-like (ico-like) particles in the system. We observe that both the abundance of ico-like clusters and their chemical composition vary non-monotonically with concentration. Besides, chemical composition of ico-like clusters is found to be deviated significantly from the mixing ratio at $\alpha > 0.25$; relative lacks of copper atoms vary in the range $6 \div 12\,\%$ with non monotonic dependence on α.

For the molecular dynamics (MD) simulations, we used LAMMPS package [1]. The system of $N \approx 5000$ particles was simulated under periodic boundary conditions in Nose–Hoover NPT ensemble at pressure $P = 1$ atm. Initial configurations were equilibrated melts at $T = 1200$ K. The system was cooled down to $T = 300$ K with the cooling rate $\gamma = 10^{11}$ K/s. Interactions between alloy components is described here using widely accepted embedded atom potential specially adopted for liquid and glassy Cu−Zr system [2].

The BOOP method [3] is widely used in condensed matter physics to quantify the local orientational order. The method allows us to explicitly recognize symmetry of local atomic clusters (e.g. [4]) and study their spatial distribution [5].

For BOOP investigation we define the rotational invariants (RI) of rank l of the second order q_l and third order w_l. The advantage of q_l and w_l is that they are uniquely determined for any polyhedron including the elements of any crystalline structure. Among the RI, q_4, q_6, w_4, w_6 are typically the most informative ones so we use they in this work. To identify ico-like clusters we calculate the rotational invariants q_l and w_l for each atom using the fixed number of nearest neighbors ($N_{\rm nn} = 12$). Atom whose coordinates in the space (q_4, q_6, w_4, w_6) are sufficiently close to those of the perfect structures is counted as ico-like (fcc-like, hcp-like) etc.

To quantify the local order we use the normalized one-dimensional probability density function over different rotational invariants $P(q_l)$ and $P(w_l)$, so that (for, e.g., q_l) we have $\int_{-\infty}^{\infty} P(q_l)dq_l \equiv 1$. Even more convenient is using (cumulative) distribution functions associated with the $P(q_l)$ and $P(w_l)$ [4] which are defined as (by using as example the bond order parameter q_6): $C_q(x) = \int_{-\infty}^{x} P(q_6)dq_6$. Using the cumulative functions we can find abundance (density) of any solid-like structure with given accuracy $\delta_{\rm cr}$: $C_q(q^{\rm cr}+\delta_{\rm cr}) - C_q(q^{\rm cr}-\delta_{\rm cr})$, where $q^{\rm cr}$ is the bond order parameter for the given lattice type.

We note, that the set of distributions P and C taken for different q_l and w_l completely describes the local

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orientational order in the system as an abundance of different ordered and disordered structures. Behaviour of the distributions $P(q_6)$, $P(w_6)$ and $C(q_6)$, $C(w_6)$ in the vicinity of the perfect icosahedron (having $q_6^{\rm ico} \approx \approx 0.66$ and $w_6^{\rm ico} \approx -0.17$ clearly shows non monotonic dependence of density of ico-like atoms on α value. For instance, at considered cooling rate ($\gamma = = 10^{11}$ K/s), the maximum density of ico-like clusters occurs at $\alpha = 0.785$. To better illustrate such non monotonic behaviour, we show in Fig. 1 the dependence of

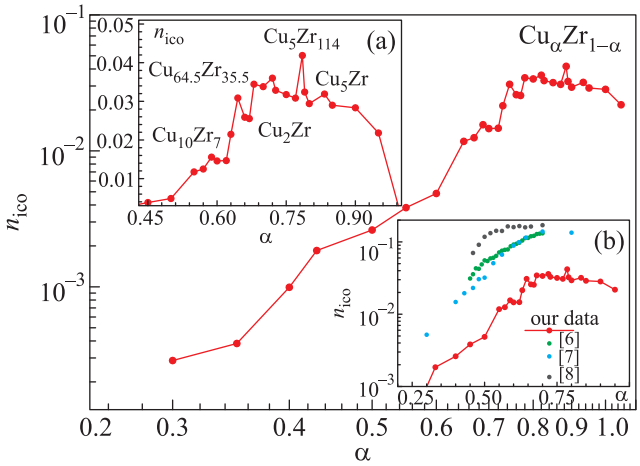

Fig. 1. (Color online) Simulated $Cu_\alpha Zr_{1-\alpha}$ alloy at $T = = 300$ K. Main frame: abundance of ico-like clusters $n_{\rm ico}$ versus copper abundance α. Non monotonic behavior of the ico-like cluster density is seen at $\alpha \geq 0.5$. Left inset (a) shows the fine details of $n_{\rm ico}(\alpha)$ dependence in the range $\alpha > 0.45$. Right inset (b) shows comparison of our $n_{\rm ico}(\alpha)$ dependence with those obtained by other authors [6–8]

the abundance of ico-like clusters $n_{\rm ico}$ on Cu concentration α. A cluster is treated as ico-like one if it has order parameters $q_6 > 0.6$ and $w_6 < -0.16$. We see that $n_{\rm ico}(\alpha)$ is essentially non monotonic with maximal amount of ico-like clusters within the range $0.6 < < \alpha < 0.9$. Moreover, $n_{\rm ico}(\alpha)$ demonstrates local extrema located at stoichiometry compositions of a few Cu–Zr intermetallic compounds as well at the BMG composition $Cu_{0.645}Zr_{0.355}$. The presence of such extrema correlates with the existence of pinpoint compositions of BMG formation in real Cu−Zr alloys. Indeed, the ranges of local $n_{\rm ico}(\alpha)$ maxima are expected to correspond to high GFA compositions. The very fact that simple EAM model potential can describe such nontrivial behaviour (at least qualitatively) is the important result. Moreover, the maximum at $Cu_{0.645}Zr_{0.355}$ composition exactly corresponds to one of the pinpoint composition of BMG formation. So even the quantitative agreement with experimental data takes place.

In the right inset of Fig. 1 we also show the comparison of our data with those obtained in [6–8]. As seen from the picture, our $n_{\rm ico}(\alpha)$ curve demonstrates qualitatively the same behaviour as those obtained by other authors. But, quantitatively, our $n_{\rm ico}$ values are much lower then those presented in [6–8]. The main reason for such deviation is the difference of methods used to determine ico-like clusters. Our results were obtained by BOOP method but the others by VT one. Voronoi index is an topologically stable characteristic which is not sensitive to deformation of the clusters. For example, any polyhedron with the index $\langle 0, 0, 12, 0\rangle$ is treated as an icosahedron regardless of its distortion degree. That can cause the false determination of clusters structure and their abundances. That can also be the reason for the absence of local extremal in $n_{\rm ico}(\alpha)$ curves obtained by VT method.

In the paper we investigated the local orientational order of the simulated $Cu_\alpha Zr_{1-\alpha}$ metallic glass in fine detail by using bond order parameter method and found out the non monotonic behavior of the abundance of ico-like cluster versus α value. Comparison of the BOOP and Voronoi methods reveals that Voronoi method significantly overestimates the number of ico-like particles in the system. We show that abundance of the ico-like clusters and the chemical composition of these clusters are essentially non monotonic versus α and demonstrate local extrema. That qualitatively explains the existence of pinpoint concentrations of high glass-forming ability observing in Cu−Zr alloys. Finally, it has been shown that VT method overestimates drastically the abundance of the ico-like clusters in comparison with the BOOP one.

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