Structural and chemical orders in Ni$_{64.5}$Zr$_{35.5}$ metallic glass by molecular dynamics simulation

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The atomic structure of Ni$_{64.5}$Zr$_{35.5}$ metallic glass has been investigated by molecular dynamics (MD) simulations. The calculated structure factors from the MD glassy sample at room temperature agree well with the x-ray diffraction (XRD) and neutron diffraction (ND) experimental data. Using the pairwise cluster alignment and clique analysis methods, we show that there are three types of dominant short-range order (SRO) motifs around Ni atoms in the glass sample of Ni$_{64.5}$Zr$_{35.5}$, i.e., mixed-icosahedron(ICO)-cub, intertwined-cube, and icosahedronlike clusters. Furthermore, chemical order and medium-range order (MRO) analysis show that the mixed-ICO-cube and intertwined-cube clusters exhibit the characteristics of the crystalline B2 phase. Our simulation results suggest that the weak glass-forming ability (GFA) of Ni$_{64.5}$Zr$_{35.5}$ can be attributed to the competition between the glass forming ICO SRO and the crystalline mixed-ICO-cube and intertwined-cube motifs.

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I. INTRODUCTION

Atomic structures of metallic glasses (MG) have attracted considerable attention [1–8] since extraordinary properties such as strength and elasticity in MG systems are closely related to the atomic packing structures in the glasses [9]. Although MGs do not exhibit long-range translational and rotational orders, experiments [10–12] and theoretical simulations [13,14] have indicated that there are short- to medium-range orders in MGs. It is believed that the icosahedral (ICO) short-range order (SRO) is responsible for glass-forming ability (GFA) [15–17]. Meanwhile, SRO and medium-range order (MRO) also govern the mechanical response to deformation in the MG systems [18]. Hence investigating such atomic SRO and MRO structures in metallic liquids and glasses is a key to understanding the structure-properties relationship of MG materials.

Among all Ni-Zr alloys with different compositions, it is believed that Ni$_{64.5}$Zr$_{35.5}$ could be the most promising candidate for forming bulk MG, since Ni$_{64.5}$Zr$_{35.5}$ is close to a eutectic point in the Ni-Zr binary phase diagram [19–21]. Because the melting temperature is at a local minimum at the eutectic composition, the kinetics associated with crystal nucleation and growth would be relatively easily suppressed, leading to a relatively higher GFA compared to the same alloy system at other compositions. In particular, it has been shown that the critical cooling rate for glass formation is minimal for the Ni-Zr alloy containing about 35 at.% Zr [22], which suggests that Ni$_{64.5}$Zr$_{35.5}$ has the highest GFA in a Ni-Zr system. However, compared to the well-known Cu-Zr system, which has been commonly regarded as a good glass former in binary metallic alloys [23,24], experimental synthesis of bulk MG of Ni$_{64.5}$Zr$_{35.5}$ is still very challenging.

Although Ni and Cu differ only by one electron, the GFA of Cu$_{64.5}$Zr$_{35.5}$ and Ni$_{64.5}$Zr$_{35.5}$ is very different. Cu$_{64.5}$Zr$_{35.5}$ glassy samples with mm size can be fabricated by the copper mold casting method [23], while glassy Ni$_{64.5}$Zr$_{35.5}$ ribbons can only be obtained by a careful melt-spinning process [20]. The cooling rate in the melt-spinning method is typically $10^5$–$10^6$ K/s, which is much faster (about two orders of magnitude) than that of the casting method. This difference indicates that the GFA of Ni$_{64.5}$Zr$_{35.5}$ is much weaker relative to that of the Cu$_{64.5}$Zr$_{35.5}$ system. This weaker GFA nature of Ni$_{64.5}$Zr$_{35.5}$ could be attributed to the difference in the short- to medium-range order in the atomicistic structures between the two systems. For example, it is believed that a crystal-like motif can facilitate the crystal nucleation and growth to prevent the glass formation if the cooling rate is not high enough. Therefore investigating the differences of short- to medium-range ordered structure and chemical order between Ni$_{64.5}$Zr$_{35.5}$ and Cu-Zr system would provide useful insights into the origin of weak GFA in Ni$_{64.5}$Zr$_{35.5}$.

Using the experimental x-ray diffraction (XRD) and neutron diffraction (ND) experimental data, the atomic structure of Ni$_{64.5}$Zr$_{35.5}$ MG has been studied by reverse Monte-Carlo (RMC) method and Voronoi tessellation analysis [25,26]. These studies have suggested that a large number of icosahedral-like and prismaticlike SRO structures exist in Ni$_{64.5}$Zr$_{35.5}$ glass. Moreover, a significant degree of chemical ordering has also been observed in Ni$_{64.5}$Zr$_{35.5}$ glass samples [26]. However, compared to the RMC method, MD simulation has a great advantage in obtaining more reliable atomic structures as long as the interatomic potentials are accurate. Fortunately, the interatomic potential of the Ni-Zr system has been developed recently [27], which allows us to perform direct MD simulations for Ni$_{64.5}$Zr$_{35.5}$. To our knowledge,
although MD simulations for liquid Ni-Zr binary alloys have been reported [27], MD simulations of metallic glass at the composition around Ni64Zr35.5 are still lacking. Moreover, no detailed explanation of experimental results by MD simulations has been reported yet. Reliable MD simulations for this system will enable us to look into the structures of the alloy at undercooled liquid and glass states at the atomistic level, and provide very useful insights into the GFA in this system.

In this paper, the atomic structure of Ni64Zr35.5 glass is studied by MD simulations using the Finnis-Sinclair-type potential recently developed [27,28]. The pairwise cluster alignment method and clique analysis algorithm [29,30] are used to identify the dominant structure order in the MD Ni64Zr35.5 sample. This approach can extract a clique of similar clusters from the atomic structure of the MD sample without knowing the details of packing motif in advance. Meanwhile, the cluster alignment method can also calculate the populations of SRO clusters and explore the MRO in metallic liquid and glass systems. In addition to a large fraction of populations of SRO clusters and explore the MRO in metallic without knowing the details of packing motif in advance. The SROs in Ni64Zr35.5 MD samples are analyzed by the pairwise cluster alignment method [29,30]. In this method, a cluster can be assigned to each atom in the MD sample by extracting this atom and its first neighbor cell atoms along with the relevant atom species [34]. The SROs in Ni64Zr35.5 glass sample obtained from the MD simulations. Furthermore, we show that the cubic part of mixed-ICO-cube cluster and the intertwined-cube cluster have excellent chemical ordering, indicating the emergence of a metastable crystalline B2 phase [31]. Our results show that the suppression of glass formation by the crystalline B2 phase could be responsible for the weak GFA of Ni64Zr35.5.

II. METHOD

The sample used in MD simulations of Ni64Zr35.5 contains 3225 Ni and 1775 Zr atoms. The simulations are performed using the isothermal-isobaric (NPT) ensemble with the Nose-Hoover thermostat in LAMMPS code [28]. The semiempirical Finnis-Sinclair-type interatomic potential developed by Wilson and Mendeloff is employed [27]. The time step in the MD simulations is 2.5 fs. Before the cooling process, the sample is held at 2000 K for 2.5 ns to achieve equilibrium. After that, the sample is cooled down to 300 K continuously with different cooling rates at 1013, 1012, 1011, and 1010 K/s, respectively. In order to eliminate the effect of atomic thermal motions, the structural and chemical orders in the glass sample at 300 K are averaged over 500 ps, which is sufficient to obtain the convergent results for the structural and physical properties studied in this paper.

In order to compare with the experimental data, the total structure factors $S(q)$ of the Ni64Zr35.5 MD samples are calculated by the Faber-Ziman formalism [32]:

$$S(q) = \sum_{i \leq j} w_{ij} S_{ij}(q),$$  

(1)

where $i$ or $j$ denotes atomic specie. Here, the partial structure factor $S_{ij}(q)$ is

$$S_{ij}(q) = 1 + 4\pi\rho_j \int_0^\infty [g_{ij}(r) - 1] \frac{\sin(qr)}{qr} r dr,$$  

(2)

where $g_{ij}(r)$ is the partial pair correlation function and $\rho_j$ is the number density of the relevant atom specie. To compare with the XRD results, the $q$-dependent scattering factors [33]

$$w_{ij}^{\text{XRD}}(q) = (2 - \delta_{ij})c_i c_j f_i(q) f_j(q) \left[ \sum_l c_l f_l(q) \right]^2$$  

(3)

are used in the Faber-Ziman formalism, where $c_i$ and $c_j$ are the compositions of the relevant atom species and $f_i(q)$ and $f_j(q)$ are the corresponding $q$-dependent atomic scattering factors in the XRD experiment. For comparison with neutron diffraction (ND) data, we use the weighting coefficients [26]

$$w_{ij}^{\text{ND}} = (2 - \delta_{ij})c_i c_j \frac{b_i b_j}{(\sum_l c_l b_l)^2},$$  

(4)

where $b_i$ and $b_j$ are the coherent neutron scattering length of the relevant atom species [34].

The SROs in Ni64Zr35.5 MD samples are analyzed by the pairwise cluster alignment method [29,30]. In this method, a cluster can be assigned to each atom in the MD sample by extracting this atom and its first neighbor cell atoms along with it from the MD sample. Then, each cluster extracted from the MD sample is used as a template and all other clusters with the same chemical element at the center are aligned against it. The similarity between the aligned cluster and the template is measured by an alignment score defined as

$$f = \min_{0.8 < \alpha < 1.2} \left[ \frac{1}{N} \sum_{i=1}^N \left( \frac{\bar{r}_{ic} - \alpha \bar{r}_{ii}}{\sigma_{ric}} \right)^2 \right]^{1/2},$$  

(5)

where $N$ is the number of the neighbor atoms in the template. $\bar{r}_{ic}$ and $\bar{r}_{ii}$ are the atomic positions in the aligned cluster and template, respectively. To obtain optimal alignment $\alpha$ is chosen between 0.8 and 1.2 to vary the size of the template. Once we have all the alignment scores between any two clusters in the glass sample, we can obtain a clique of clusters whose pairwise alignment scores are smaller than a cutoff value of 0.15. The clusters belong to the same clique are very similar with each other and have common SRO.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the evolution of instantaneous potential energy $E$–$3k_B T$ as a function of temperature with a continuous cooling rate of $10^{10}$ K/s. In harmonic systems, the temperature dependence of both kinetic energy and potential energy are $3/2k_B T$. Therefore $E$–$3k_B T$ will be a constant for all temperatures in harmonic systems. By subtracting $3k_B T$ from the total energy obtained from MD simulations, the temperature dependence of anharmonicity in the system can be seen more clearly [35]. In particular, the plot in Fig. 1 shows that the anharmonicity in liquid and glass are different, which enables us to see the glass transition and estimate the glass transition temperature $T_g$ from the plot. From Fig. 1, one can see that at temperature higher than 975 K the energy decreases significantly with decreasing temperature, whereas at the low temperature region with $T < 975$ K the energy has only a slight decrease and is nearly constant around room temperature. Clearly, it shows a transition from liquid to glass.
and the obtained glass transition temperature is $T_g \approx 975$ K, which agrees with the experimental result [19].

In order to see how good are the glass samples obtained from our MD simulations in comparison with experiment, we calculated the total and partial structure factors using Faber-Ziman formalism [32] for the samples at 300 K prepared by different cooling rates. As shown in Figs. 2(a) and 2(b), although there is a slight shift of the height of the main peak, one can observe that the structure factors calculated from our MD simulations using Eqs. (3) and (4) agree well with the experimental XRD and ND data [26], respectively. It should be noted that as the same problem in RMC method, the agreement between the calculated and experimental $S(q)$ does not always guarantee the correct description of the three-dimensional atomistic structures in the glass sample. Nevertheless, this good agreement of total structure factors is an essential requirement of the reliable MD simulation.

We can see from Figs. 2(a) and 2(b) that the height of main peak increases with lowering cooling rate, indicating that more order is developed with lower cooling rate. In Fig. 2(b), the experimental ND data and the simulated ND spectrum exhibit a prepeak [25] around $q \approx 1.8$ Å$^{-1}$ in addition to other peaks. Because the low $q$ region in reciprocal space corresponds to large distance in real space, the prepeak would indicate certain medium-range correlations in the glass structure [36]. However, the prepeak is not well seen in the in XRD spectra from both experiment and simulation. Therefore the origin of this small prepeak needs further investigation.

The comparisons between the calculated and experimental partial structure factors [26] are shown in Fig. 3. The overall agreement between the calculated and experimental spectra are reasonably good but some discrepancies are present, especially for the partial $S(q)$ of the Zr-Zr pairs. Although the peak positions agree with each other, the peak intensity of the first peak from the calculation is much higher than that seen in experiment. It should be noted that the experimental partial structure factors are calculated from the different total structure factors of isotopic substitutions. The differences of total structure factors among the isotopic substitutions may be very small, so that the uncertainty of the obtained partial structure factors could be relatively larger. Another source of the differences may also be attributed to the inaccuracy in the interatomic potential used in the simulation, but we also would like to note that the potential has been successfully applied to explain several phenomena in Ni$_{50}$Zr$_{50}$ (see Ref. [37]). Nevertheless, the main discrepancy is in the intensity of the peak at small $q$ values, which affects the degree of MRO in the system. The peaks of Ni-Ni and Ni-Zr around $q = 3$ Å$^{-1}$ corresponding to the dominant SRO clusters in Ni$_{64.5}$Zr$_{35.5}$ agree well with experiment, suggesting the SRO results from our simulation and analysis should be reliable.

The structure analysis based on the atomistic model from our MD simulations shows that the dominant motifs around Ni and Zr atoms in Ni$_{64.5}$Zr$_{35.5}$ glass at 300 K are mixed-ICO-cube, intertwined-cube, and ICO-like clusters. The corresponding structures of mixed-ICO-cube and intertwined-cube motifs are shown in Fig. 4. In mixed-ICO-cube motif, the center Ni atom is surrounded by ten atoms. This motif can be viewed as a combination of a half-cube and a half-icosahedron as shown in Fig. 4(a). The sites (2, 3, 4, 7, 8, 9, 10) are the seven corners of a slightly distorted cube, forming three nearly orthogonal squares. On the other side, the center Ni atom is
To analyze the SRO of Zr-centered clusters. Figures 5(a) and 5(b) include the common motifs Z15 and Z16 clusters as templates. The coordination number of Zr in our sample is about 15.6, we only used pairwise alignment method other than Z15 and Z16, and the no dominant motif of Zr-centered clusters is found by the alignment scores distribution against these templates. Since clusters extracted from the MD samples to calculate the crystalline motifs such as bcc, fcc, and hcp motifs as templates, the other portions of surfaces are ten triangles constituting a slightly distorted half-ICO. (b) Intertwined-cube cluster can be viewed as two interpenetrating cubes with common (111) plane formed by sites (Zr3, Zr4, Zr5). The sites (Ni3, Ni4, Ni5, Zr2, Zr3, Zr4, Zr5) and (Ni1, Ni2, Ni6, Zr1, Zr3, Zr4, Zr5) form the two half-cubic surfaces C1 and C1′, respectively. Here, the usage of Ni or Zr as the site’s name is to imply that the corresponding sites could be mostly occupied by Ni or Zr as revealed in the following investigation.

FIG. 3. Partial structure factors of (a) Ni-Ni, (b) Ni-Zr, and (c) Zr-Zr for Ni64.5Zr35.5. In spite of some differences between calculated MD simulations and experimental data, the peaks of Ni-Ni and Ni-Zr around \( q = 3\) Å\(^{-1}\) corresponding to the dominant SRO clusters in Ni64.5Zr35.5 only have some minor deviations.

Also enclosed by ten triangles, which form the surface of a half slightly distorted icosahedron. Similarly, the intertwined-cube motif can be regarded as two interpenetrating cubes C1 and C1′ sharing a common (111) plane as shown in Fig. 4(b). Thus the center Ni atom in intertwined-cube cluster is surrounded by 6 faces (11 atoms), which form two groups of nearly orthogonal squares. By contrast, ICO-like clusters in our MD samples (not shown) are nearly identical to the ideal ICO motif, with only slightly distortions.

After identifying the dominant structure motifs in the glass sample, we take these three motifs along with some common crystalline motifs such as bcc, fcc, and hcp motifs as templates and perform cluster-template alignment for all the Ni-centered clusters extracted from the MD samples to calculate the alignment scores distribution against these templates. Since no dominant motif of Zr-centered clusters is found by the pairwise alignment method other than Z15 and Z16, and the coordination number of Zr in our sample is about 15.6, we only use the common motifs Z15 and Z16 as templates to analyze the SRO of Zr-centered clusters. Figures 5(a) and 5(b) show the distribution of alignment scores for Ni- and Zr-centered clusters from MD glass sample at 300 K, respectively. As shown in Fig. 5(a), compared to the other motifs of Ni-centered cluster, the distribution of scores for mixed-ICO-cube, intertwined-cube, and ICO-like motifs have relatively larger portion in the region with small score. It indicates that the local structures in the sample can be better described by these motifs than the others. Similarly, Fig. 5(b) shows the Z15 cluster is the major motif of Zr-centered cluster in Ni64.5Zr35.5.

To describe the SRO of glass sample quantitatively, we use an alignment score 0.15 as a cutoff to assign the clusters to the given template. If a cluster has an alignment score less than 0.15 for more than one template, the lowest alignment score is used to assign the motif of the cluster. The choice of cutoff value of 0.15 for determining the fraction of the SRO motif is a bit arbitrary but it is guided by considering the thermal motion of the atoms at given temperature. This cutoff value is inferred from the width of the first peak in the calculated pair correlation \( g(r) \), which reflects the atomic displacements due to thermal motion. At 300 K, the width of the first peak of \( g(r) \) is roughly 0.15 \( d_0 \), where \( d_0 \) is the averaged nearest-neighbor bond length.

Table I shows the fractions of SROs in the glass sample at 300 K prepared by continuous cooling of 10\(^{10} \) K/s. As a result, we found that the fractions of Ni-centered mixed-ICO-cube, intertwined-cube, and ICO-like motifs in the Ni64.5Zr35.5 glass sample at 300 K are 18.6%, 9.3%, and 11.8% of the total Ni atoms, respectively. By contrast, the fraction of Zr-centered Z15 motif is only about 4.8% of total Zr atoms. Other kinds of Ni (Zr) centered motifs such as bcc, fcc, and hcp have less than 5% of the total Ni (Zr) atoms. Since the populations of these minority motifs are much less than those of the dominant motifs around the Ni central atoms, such minority motifs will be ignored in the following discussions.

From the alignment score distributions shown in Fig. 5, we can see that different choice of the cutoff value will change the fraction numbers of the motifs, but the relative ratios among different motifs are not sensitive to the choice of cutoff value as long as this value is reasonably chosen. Therefore our conclusion that the...
mixed-ICO-cube, intertwined-cube, and ICO-like motifs are dominating the atomistic SRO in the glassy sample does not depend on the choice of cutoff score.

Moreover, although only about 40% of the Ni atoms can be classified as the central atoms of the three dominant motifs under the cutoff score of 0.15, the total number of atoms involved in the first shells of these dominant clusters is about 95% of the total atoms in the sample. Therefore the local structures in the system are dominated by the Ni-centered mixed-ICO-cube, intertwined-cube, and ICO-like motifs. In fact, if we choose the cutoff value of 0.18 for the Ni-centered clusters, about 86% of Ni atoms can be assigned and the relative ratios among the above three motifs are almost the same as that with the cutoff score of 0.15. The relative fractions of the bcc, fcc, and hcp clusters are still very small. This result indicates that the local orders around the Ni atoms in the glass sample are similar to mixed-ICO-cube, intertwined-cube, and ICO-like clusters.

In comparison with the binary Cu$_{64.5}$Zr$_{35.5}$, which has much stronger GFA than Ni$_{64.5}$Zr$_{35.5}$, our MD simulation results show that the fraction of ICO-like cluster in Ni$_{64.5}$Zr$_{35.5}$ is much less than that in Cu$_{64.5}$Zr$_{35.5}$ [38]. It suggests that the ICO cluster indeed plays an important role in glass formation in intermetallic systems. The difference in the ICO fraction in the two systems can be attributed to the strong hybridization between Ni-Zr d electrons, which is much weaker in Cu-Zr systems, as demonstrated by previous ab initio MD simulation studies [39,40].

Chemical order is also a useful parameter to describe and predict the GFA in many alloys. To characterize the chemical order in our MD glass samples, all the clusters with the alignment score $<0.15$ to a given template are superposed by overlapping the center Ni atoms and keeping the orientation as that at the best alignment position. As shown in Figs. 6(a)–6(c), one can observe that the collective alignment of these clusters gives a pattern of the template, where the red and blue spheres denote Ni and Zr atoms, respectively. In order to calculate the chemical occupation probability, we count the percentage of the Ni and Zr atoms at each site, after all the aligned clusters are overlapped together. Figures 6(d)–6(f) are the calculated occupation probabilities of Ni or Zr on the sites of templates. For mixed-ICO-cube clusters, the atoms 2, 3, 4, 7, 8, 9, and 10 can be counted as cube atoms. Our results show that the chemical composition at sites 2, 4, 8, 10 is Ni-rich (although it is a bit weak in site 8), while at sites 3, 7, 9 is Zr-rich, exhibiting the trend of B2 chemical order. At the other sites of the cluster, Ni and Zr concentrations are close to the stoichiometry of Ni$_{64.5}$Zr$_{35.5}$. This trend of B2 chemical order is even more pronounced in the intertwined-cube clusters as shown in Figs. 6(b) and 6(e). The weaker chemical order in the mixed-ICO-cube motif as compared to that in the intertwined-cube motif would be due to the mix of ICO structure in the mixed-ICO-cube motif. By contrast, the Ni and Zr concentrations at each site of the ICO-like clusters are close to the stoichiometry of Ni$_{64.5}$Zr$_{35.5}$, as one can see from Figs. 6(c) and 6(f). From this analysis, we can see that all the sites with pronounced chemical order are associated with the cubic corners of templates. These sites with excellent chemical order can be viewed as the “genes” of crystal-like phase. The emergence of such crystalline genes even when the sample is quenched at very fast cooling rates could be responsible for the weak GFA in the Ni$_{64.5}$Zr$_{35.5}$ sample.

We also examined the MRO around the mixed-ICO-cube and intertwined-cube SRO clusters. By overlapping the center atoms of the same SRO clusters and keeping the orientation of the clusters at the positions from the SRO alignment with a given template, we can see the alignment distribution of the atoms in the second shell of these clusters. As shown in Fig. 7(a), we can see that the atoms in the second shell of the mixed-ICO-cube clusters resemble the B2 structure. In particular, one can observe that the second shell sites are mostly...
investigate the effects of sub-$T_g$ glass phase formation in the Ni$_{64}$ and intertwined-cube cluster, suggesting the suppression of cube clusters are Ni. These MRO results demonstrate a certain around these bcc-lattice sites in the second shell of intertwined-mixed-ICO-cube motif, we found that the majority of the atoms in the intertwined-cube clusters. Our results demonstrate that the crystallinility clusters have much more pronounced chemical order than that of ICO, implying that the crystalline phase could still emerge in the Ni$_{64}$Zr$_{35.5}$ sample even by the fast cooling process.

occupied by Ni atoms, indicating excellent chemical order of B2 crystal fragment. Similarly, the atoms of the second shell around the intertwined-cube cluster centers are also arranged in a bcc-like lattice, as shown in Fig. 7(b). Like in the case of mixed-ICO-cube motif, we found that the majority of the atoms around these bcc-lattice sites in the second shell of intertwined-cube clusters are Ni. These MRO results demonstrate a certain degree of crystal nucleation ability from the mixed-ICO-cube and intertwined-cube cluster, suggesting the suppression of glass phase formation in the Ni$_{64.5}$Zr$_{35.5}$ sample. Recently, it has been demonstrated that performing MD simulated annealing below but close to the glass transition temperature (i.e., sub-$T_g$ annealing) can accelerate structural relaxation since the structural relaxation and glass formation is much more efficient in the vicinity of $T_g$ [38,41,42]. To investigate the effects of sub-$T_g$ annealing in Ni-Zr systems, the initial Ni$_{64.5}$Zr$_{35.5}$ sample at 2000 K is continuously cooled down to 925 K at $10^{10}$ K/s, then the as-quenched sample is annealed for 1400 ns at 925 K. Finally, the annealed sample was continuously cooled down to 300 K at $10^{10}$ K/s. The MD steps used for such a cooling-annealing-cooling cycle is equivalent to a cooling rate of $1.08 \times 10^9$ K/s. Figure 8(a) shows the potential energy at 300 K for different cooling rates including the result from the sub-$T_g$ annealing cycle. It can be seen that the potential energy for the samples with continuous cooling linearly depends on the logarithm of cooling rates, which is similar to the case of other binary alloy systems such as Cu-Zr [41], Al-Sm [42], and Ni-Nb [43]. When considering the error bar of the fitting, the potential energy for Ni$_{64.5}$Zr$_{35.5}$ from the sub-$T_g$ annealing simulation is actually not far away from the extrapolation of the least-square fitting line based on the energies of the continuously cooled samples. This result suggests that in order to get the same potential energy, the simulation time used for sub-$T_g$ annealing is almost the same as that used in continuously cooling. This result is very different from the case of a strong glass forming system like Cu$_{64.5}$Zr$_{35.5}$, where the sub-$T_g$ annealing approach can help to speed up the glass formation process [41]. Our results indicate that in a weak glass forming system like the present case of Ni$_{64.5}$Zr$_{35.5}$, sub-$T_g$ annealing is not very effective owing to the relatively stronger crystalline nucleation tendency.

To study the influence of cooling rate on the SRO clusters, we show the fractions of mixed-ICO-cube, intertwined-cube, and ICO-like clusters in the sample of 300 K with different cooling rates in Fig. 8(b). When the cooling rate is lowered, the fraction of ICO-like clusters is nearly constant while that of intertwined-cube clusters increases considerably. The fraction of the mixed-ICO-cube clusters also increases slightly with lowering the cooling rate. The open symbols shown in Fig. 8(b) are the fractions of SRO clusters for the samples after the sub-$T_g$ annealing process with an effective cooling rate of $1.08 \times 10^9$ K/s. Since the intertwined-cube cluster has the character of a crystalline phase while the ICO-like cluster is more related to a glass phase, our results suggest that even in the very fast quench process the crystalline phase motifs are still the dominant SRO in the Ni$_{64.5}$Zr$_{35.5}$ system. Therefore Ni$_{64.5}$Zr$_{35.5}$ should not be a good glass former.

To further investigate the competition among different SRO motifs, we also examine the evolution of SRO clusters during the sub-$T_g$ annealing at 925 K. During the annealing process, for every 200 ns, the sample is quenched to 10 K to obtain the inherent structure for SRO analysis. Figure 8(c) shows the evolution of fractions of mixed-ICO-cube, intertwined-cube, and...
Fig. 8. (a) The potential energy of Ni$_{64.5}$Zr$_{35.5}$ at 300 K for different cooling rates. (b) The fractions of mixed-ICO-cube, intertwined-cube, and ICO-like clusters in Ni$_{64.5}$Zr$_{35.5}$ at 300 K for different cooling rates. With lower cooling rate, the fraction of the intertwined-cube cluster that represents a crystalline phase increases while the fraction of ICO-like cluster is nearly constant, suggesting the suppression of the glass phase formation by the competitors (crystalline phase) in the Ni$_{64.5}$Zr$_{35.5}$ sample. (c) The evolution of fractions of mixed-ICO-cube, intertwined-cube, and ICO-like clusters during the annealing process at temperature 925 K. One can observe that there is a clear phenomenon of competition between the representation of crystalline phase (intertwined-cube cluster) and the glass phase (ICO-like cluster).

IV. CONCLUSIONS

In summary, the atomic structure of Ni$_{64.5}$Zr$_{35.5}$ alloy has been studied by MD simulations combined with the cluster Alignment method analysis. The calculated total structure factors agree well with the XRD and ND scattering experimental data. By pairwise cluster alignment and clique analysis, we found three kinds of Ni-centered motifs are the dominant SRO in the Ni$_{64.5}$Zr$_{35.5}$ sample at 300 K, i.e., mixed-ICO-cube, intertwined-cube, and ICO-like cluster. The mixed-ICO-cube motif has half-ICO and half-cube structure. The intertwined-cube cluster is constituted of two interpenetrating slightly distorted cubes with common (111) plane. The ICO-like cluster is very close to an ideal ICO with slight distortion. Meanwhile, the fractions of the other kinds of Ni-centered motifs and all Zr-centered motifs are much smaller than those of the above three dominant motifs.

In addition, we also analyze the chemical order of the three dominant SRO clusters by directly evaluating the occurrence probability of Ni (Zr) atoms around each sites of the SRO cluster. Our results show that the cubic portion of mixed-ICO-cube and the whole intertwined-cube clusters have excellent chemical order, implying the emergence of crystalline motifs in the Ni$_{64.5}$Zr$_{35.5}$ alloy even in fast cooled samples. Furthermore, we studied the MRO of the mixed-ICO-cube and intertwined-cube clusters and found that around the bcc centers there is a high probability of finding another Ni atom at the second shell from the central Ni atom. This suggests that the mixed-ICO-cube, intertwined-cube clusters have the character of crystalline a metastable B2 phase in the Ni-Zr system. We also found that the fraction of the intertwined-cube cluster increases with lowering cooling rate while that of the ICO-like cluster remains constant, implying that the glass formation would be suppressed by the small crystalline fragments of the B2 phase. The evolution of SROs with the annealing time also shows competition between intertwined-cube and ICO-like clusters. Our results suggest that the weak GFA can be attributed to the existence of SROs with crystalline character in the Ni$_{64.5}$Zr$_{35.5}$ alloy.

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[40] Y. Huang, L. Huang, C. Z. Wang, M. J. Kramer, and K. M. Ho, Comparative study of local atomic structures in Zr2CuNi1−x (x = 0, 0.5, 1) metallic glasses, J. Appl. Phys. 118, 195902 (2015).

