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Abstract
High-resolution x-ray diffraction experiments were performed for $Zr_{70}Cu_{30-x}Pd_x$ (x = 0, 1, 5, 10, 20 and 30 at.%) metallic glasses together with reverse Monte Carlo. A pre-peak arising in the low-Q range of $S(Q)$ in $Zr_{70}Cu_{29}Pd_1$ metallic glass was detected whereas no pre-peak was observed in the other samples. The origin of the pre-peak is identified to be the medium-range order around Pd atoms occupying an octahedral-like cluster in the metallic glass. When a pre-peak in $S(Q)$ exists for metallic glasses containing heavy metal elements at a low concentration (such as noble metal or rare earth elements), medium-range order, centered with these heavy atoms, might occur in metallic glasses.

Since the discovery in the early 1990s of new glassy systems, based on multi-component alloys, bulk metallic glasses (BMGs; with thickness larger than 1 mm) have been extensively studied because of their extraordinary mechanical and magnetic properties [1–11]. Considerable work has been devoted to exploring the atomic structure of BMGs by means of both experimental and theoretical methods. For example, the topological-packing model was used to describe metallic glasses based on R^*, an optimum ratio between the size of the solute atom and the average size of the surrounding solvent atoms [12, 13]. Studies using a combination of x-ray diffraction (XRD) and extended x-ray absorption of fine structure (EXAFS) with reverse Monte Carlo (RMC) to investigate atomic structures of metallic glasses have been reported [14, 15]. A complete understanding of the atomic structure in metallic glasses is still lacking. One case is the pre-peak detected in the structural factor $S(Q)$ for some metallic glasses (e.g. Al-based metallic glasses) [16–19]. In amorphous or liquid samples, a pre-peak in $S(Q)$ is usually attributed to the strong chemical short-range order [20], compound-forming behavior or cluster structure between unlike atoms [21–24]. However, until now, little experimental

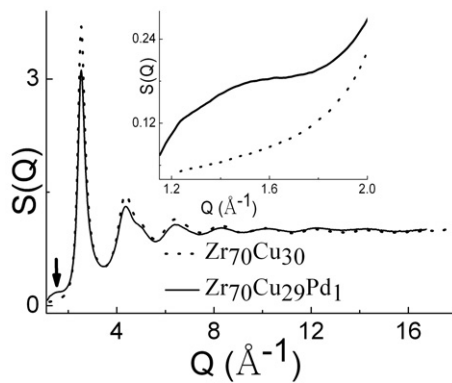[4] Author to whom any correspondence should be addressed.

Figure 1. Comparison of the structure factor $S(Q)$ in as-prepared $Zr_{70}Cu_{29}Pd_1$ (solid line) and $Zr_{70}Cu_{30}$ (dashed line) metallic glasses. A pre-peak located at about 1.4 Å^{-1} is marked by the arrow and highlighted in the inset.

evidence has been provided to support either supposition. Here we report high-resolution XRD measurements of $Zr_{70}Cu_{30-x}Pd_x$ ($x = 0, 1, 5, 10, 20$ and 30 at.%) metallic glasses. A pre-peak in $Zr_{70}Cu_{29}Pd_1$ metallic glass was detected, which was explained by the medium-range order around Pd atoms in the glass.

$Zr_{70}Cu_{30-x}Pd_x$ ($x = 0, 1, 5, 10, 20$ and 30 at.%) ingots were prepared by arc melting high-purity metals (99.8% Zr, 99.95% Cu, 99.9% Ni, and 99.9% Pd). Amorphous ribbons with a cross section of 0.03×2 mm^2 were obtained from these alloys by single-roller melt spinning at a wheel surface velocity of 30 m s^{-1} in a purified Ar atmosphere. The oxygen content of the as-prepared ribbon samples was analyzed to be less than 800 ppm by mass by inductively coupled plasma spectroscopy. The influence of oxygen on the transformation behavior can thus be disregarded.

Room-temperature high-resolution XRD measurements were carried out for all samples with high-energy x-rays (100 keV) at beamline BW5 at HASYLAB in Germany. Diffraction patterns were recorded by a Mar2300 image plate. The beamstop was located at a place away from the center to record data with a larger Q (wavevector transfer) range, resulting in high resolution for real-space the reduced pair distribution function $G(r)$. XRD patterns were obtained by integrating the Q-space data file after subtracting their background with the program Fit2D [25]. Data were then normalized by the program PDFgetX to remove the effect of polarization, sample self-absorption, the fluorescence contribution and inelastic scattering. Finally, the structure factor $S(Q)$ was obtained by using the Faber–Ziman equation [26] and truncated at both ends, leaving the region with a reliable oscillation signal. The corresponding $G(r)$ was obtained by Fourier transformation of $S(Q)$.

Figure 1 shows $S(Q)$ patterns for as-prepared $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$ metallic glasses. A hump (marked by the arrow and highlighted in the inset), located at about 1.4 Å^{-1} in Q space, before the main peak, located at about 2.5 Å^{-1}, was observed for the as-prepared $Zr_{70}Cu_{29}Pd_1$ sample whereas only a smoothly sunken curve in the same Q region was detected for the $Zr_{70}Cu_{30}$ sample. This means that a pre-peak exists in the $Zr_{70}Cu_{29}Pd_1$ sample. In order to be sure that the pre-peak is an intrinsic feature of the sample, we carried out the following experiments: (1) the XRD experiment was repeated and found no difference after the same standard procedures of data reduction; (2) glass capillaries with different diameters were used as sample containers. It was found that sample holder does not affect the pre-peak. Thus, we conclude that the observed pre-peak is indeed an intrinsic feature of the $Zr_{70}Cu_{29}Pd_1$ sample.

In our previous EXAFS work for $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$ metallic glasses [27, 28], it was found that in the as-cast amorphous state, icosahedral short-range order was detected in both samples and long-range ordered icosahedral quasicrystal phase was detected during
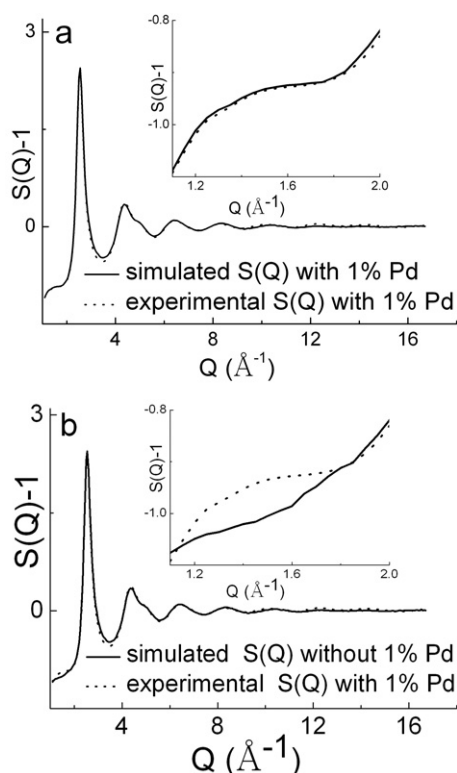
Figure 2. Comparison of RMC simulated $S(Q)$ and the experimental one (a) based on a box of 20 000 Zr, Cu and Pd atoms for the $Zr_{70}Cu_{29}Pd_1$ sample and (b) after removing the Pd atoms. A solid line is plotted for simulated $S(Q)$ while the dotted line is for the experimental one. Details are shown in the insets.

the annealing process only in the $Zr_{70}Cu_{29}Pd_1$ metallic glass, while only the intermetallic compound, Zr_2Cu phase, was crystallized in the binary $Zr_{70}Cu_{30}$ alloy. The minor Pd atoms in the metallic glass do not substitute Zr and/or Cu atoms. They are diagnosed to be centered in octahedral-like (OL) interstices among the icosahedral-like (IL) clusters in the $Zr_{70}Cu_{29}Pd_1$ metallic glass. This causes an enhancement of interaction between icosahedral clusters. Consequently, a long-range ordered icosahedral quasicrystal phase can be grown during annealing treatments in the $Zr_{70}Cu_{29}Pd_1$ metallic glass. Then, two questions are raised: (1) do 1 at.% Pd atoms really affect the pre-peak phenomenon in the metallic glass and (2) if so, how do Pd atoms contribute to the pre-peak?

To answer the two questions, we performed RMC simulation [29–32] of $S(Q)$ for $Zr_{70}Cu_{29}Pd_1$ metallic glass. Before the simulation, a box containing 20 000 atoms, according to its composition and the hard sphere dense-packed model, was built. Least-square fitting of normalized $S(Q)$ by the program RMCA was carried out under the constraint of atomic densities calculated from experimental $G(r)$ [33], which are about 0.0506 and 0.0508 Å^{-3} for $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$, respectively. Figure 2 shows the RMC results for $Zr_{70}Cu_{29}Pd_1$. It is clear that the RMC simulation fits experimental $S(Q)$ data well in figure 2(a), as magnified in the inset. The obtained atomic configuration is shown in figure 3(a). The next step is that we just removed all the Pd atoms (figure 3(b)), i.e. created some voids inside the box (figure 3(c)), and calculated $S(Q)$ by constraining all other parameters. The result is shown in figure 2(b). It is found that the calculated $S(Q)$ drops quickly in the low-Q range (details can be observed in the inset), to be similar to the $S(Q)$ observed in binary $Zr_{70}Cu_{30}$ metallic glass. These results obtained from RMC simulation for $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$ metallic glasses strongly support the scenario that the observed pre-peak in the $Zr_{70}Cu_{29}Pd_1$ metallic glass is indeed due to the Pd atoms.
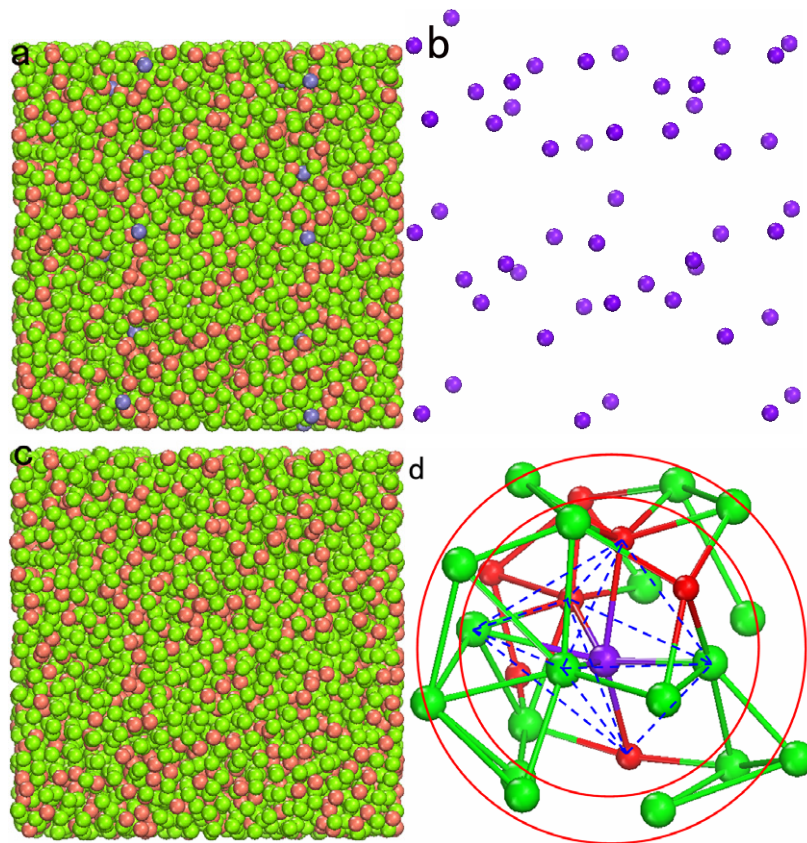
Figure 3. Atomic configurations obtained from the RMC simulation of experimental $S(Q)$ for $Zr_{70}Cu_{29}Pd_1$ metallic glass (a). (b) Atomic configuration of pure Pd atoms in (a). (c) Atomic configuration after removing the Pd atoms. (d) Atomic configuration around one Pd atom; the OL cluster is illustrated by the blue dashed lines together with the two red circles confining interatomic distances of Pd–M from 4.4 to 5 Å. Zr, Cu, Pd atoms are green, red and purple, respectively.

(This figure is in colour only in the electronic version)

To reveal how Pd atoms contribute to the pre-peak, the atomic configuration in figure 3(a) was further analyzed by the Voronoi tessellation method [34, 35]. Various Voronoi clusters (VCs) could be obtained by setting the maximum interatomic distance to be 3.5 Å. Based on such VCs around Pd atoms, it is found that Pd–M (M = Zr and Cu) pairs are divided into two regions: 2.4–2.9 Å and 3.15–3.5 Å with average coordination numbers of 5.8 and 4.7 atoms, respectively. This strongly supports the result reported in [28] that Pd atoms in the $Zr_{70}Cu_{29}Pd_1$ metallic glasses have a nearest neighbor coordination number of about 6, as in Pd-centered OL clusters. Such an OL cluster is indeed detected in the atomic configuration obtained by the RMC, marked by dashed lines in figure 3(d). Furthermore, the average atomic distance of a Pd–Pd pair is found to be 7.6 Å from the atomic configuration in figure 3(b). The pre-peak is located at about 1.4 Å^{-1} in $S(Q)$ and its corresponding average distance in $g(r)$ (pair distribution function) is about $2\pi/Q = 4.5$ Å. In our previous work [27], it was found that in both as-prepared $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$ metallic glasses, local structures of M (M = Zr or Cu) atoms are similar. Thus, if the pre-peak was caused by the local structures of M (M = Zr or Cu) atoms, then the pre-peak would be detected in both $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$ metallic
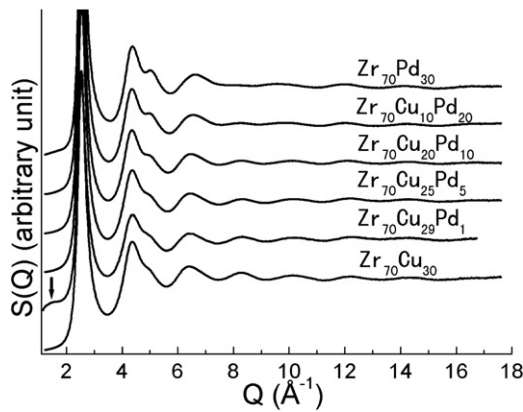
Figure 4. Structure factor $S(Q)$ of as-prepared $Zr_{70}Cu_{30-x}Pd_x$ (x = 1, 5, 10, 20 and 30 at.%) metallic glasses. The pre-peak is only detected in the $Zr_{70}Cu_{29}Pd_1$ sample, marked by the arrow.

glasses. This is not true in figure 1. From the present RMC simulation, the average atomic distance of the Pd–Pd pair was calculated to be 7.6 Å, which differs from 4.5 Å. This fact reveals that the contribution of Pd–Pd pairs should not be the main factor for the pre-peak. On the other hand, many Pd–M pairs (M = Zr or Cu, whose atoms are located at average distances of about 4.4 and 5.0 Å) are detected, as illustrated in the circles in figure 3(d). Among them, about 33% of the M atoms are the central atoms of IL clusters, which are around Pd atoms, confirming the OL cluster connection between IL clusters. Thus, we believe that the pre-peak observed in the as-cast $Zr_{70}Cu_{29}Pd_1$ metallic glass could be caused by medium-range order around Pd atoms (in the range of 4.4–5 Å). In an $Al_{90}Fe_5Ce_5$ metallic glass [36], a Fe-centered icosahedral structural unit was suggested to cause the observed pre-peak. However, this explanation cannot be the reason in the present system because IL polyhedra exist in both as-prepared $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{29}Pd_1$ [27] and no pre-peak exists in the former.

Furthermore, we also performed high-resolution XRD measurements for $Zr_{70}Cu_{30-x}Pd_x$ (x = 5, 10, 20 and 30 at.%) in figure 4. No pre-peak was detected in any of the samples. This fact can be explained as follows: in binary $Zr_{70}Pd_{30}$ metallic glass, an IL cluster-network is also presented [27, 37, 38]. The number of OL interstices, which are large enough to hold Pd atoms, is limited in the IL cluster-network, considering the 1–2% density deviation between amorphous alloys with their corresponding crystalline ones. When the Pd concentration in $Zr_{70}Cu_{30-x}Pd_x$ metallic glasses increases, most Pd atoms thus locate on the shell or at central positions of the IL clusters. This could degrade the medium-range packing order around the Pd atoms. The lower the degree of medium-range order packing, the less the contribution of Pd–M pairs to the pre-peak. Consequently, no obvious pre-peak will be detected in the samples containing greater amounts of Pd in $Zr_{70}Cu_{30-x}Pd_x$ (x = 5, 10, 20 and 30 at.%), as observed in figure 4. More studies are required to uncover what kind of medium-range order exists around the Pd atoms in the $Zr_{70}Cu_{29}Pd_1$ metallic glass.

In conclusion, the origin of the pre-peak in the low-Q range of $S(Q)$ in $Zr_{70}Cu_{29}Pd_1$ metallic glass was investigated together with $Zr_{70}Cu_{30-x}Pd_x$ (x = 0, 5, 10, 20 and 30 at.%) samples by high-resolution XRD and RMC. It is found that in $Zr_{70}Cu_{29}Pd_1$ metallic glass the Pd atoms occupying octahedral-like interstices could form Pd–M (M = Zr or Cu) interatomic correlation of medium-range (about 4.5 Å) order, which contributes to the pre-peak in $S(Q)$ for $Zr_{70}Cu_{29}Pd_1$ metallic glass at about 1.4 Å^{-1}. When the medium-range order is destroyed, no pre-peak exists in the samples containing greater amounts of Pd in $Zr_{70}Cu_{30-x}Pd_x$ (x = 5, 10, 20 and 30 at.%). We believe that when a pre-peak in $S(Q)$ exists for metallic glasses containing heavy metal elements at low concentration (such as noble metals or rare earth

elements), medium-range order, centered with such atoms, might occur in metallic glasses. This work extends our understanding of atomic structures for a body of metallic glasses.

Acknowledgments

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