Effect of thermal annealing on the local structure in ZrCuAl bulk metallic glass

Akito Ishii [a], Akihiro Iwase [a], Yuka Fukumoto [a], Yoshihiko Yokoyama [b], Toyohiko J. Konno [b], Fuminobu Hori [a,*]

[a] Department of Materials Science, Osaka Prefecture University, 1-1, Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan
[b] Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

The relaxation and crystallization behaviors of the ternary $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass were investigated by the positron annihilation measurements and the extended X-ray absorption fine structure (EXAFS) analysis at the Zr K-edge. The result of positron annihilation coincidence Doppler broadening (CDB) for as-prepared specimen suggests that the fraction of Zr atom around free volume is greater than that of composition for alloy system. According to the results of CDB spectrum and Fourier transformed EXAFS spectrum, the isothermal annealing below the glass transition temperature (T_g) (structural relaxation) decreases the size of free volume, but it causes little change in the distribution of atoms, either around free volume or around Zr atoms. For the isothermal annealing above crystallization temperature (T_x), the XRD and EXAFS spectra clearly show the crystallization of specimens. The CDB result also suggests the crystallization. These results demonstrate that the chemical order around free volume is dissociated, and crystallized order is newly formed during the thermal annealing above T_x.

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1. Introduction

Ternary $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glasses (BMGs) have a good glass forming ability, so that much attention has been paid to various applications of these alloys [1]. It is well known that the structural relaxation below the glass transition temperature (T_g) and the crystallization above the crystallization temperature (T_x) are correlated with the free volume change [2] and they affect some mechanical and physical properties [3]. Therefore, the study of relaxation and crystallization is very important in terms of engineering aspects and glass science. The formation of the local structure, such as icosahedral-phase, has been reported so far in some Zr-based alloy systems such as Zr–Cu–Ti–Ni [4] and Zr–(Pd or Pt) [5]. Recently, the relaxation process in Zr-based alloys has been reported by the positron annihilation lifetime measurement [6], the differential scanning spectroscopy (DSC) [7] and the macroscopic density measurements [8], in terms of free volume theory. However, the relationship between the atomic motion around the free volume and the local atomic structure during structural relaxation and crystallization has never been clarified yet. Generally, positron annihilation coincidence Doppler broadening (CDB) measurement has been applied to evaluate the local elemental analysis. For example, small size Cu clusters (from 2 to 3 cluster to nm size precipitate) in iron matrix can be detected, even though their structures of Cu cluster are fcc or bcc [9]. On the other hand, the extended X-ray absorption fine structure (EXAFS) measurement is another useful method for the analysis of the atomic structure of amorphous materials, because EXAFS gives us the information about the local atomic structure around selected species. Therefore, we applied positron annihilation CDB technique to estimate elemental analysis around free volume and EXAFS measurement to estimate the local atomic combination in amorphous alloy.

In this paper, the mechanism of structural relaxation and crystallization for $Zr_{50}Cu_{40}Al_{10}$ BMG is discussed from the viewpoint of local atomic ordering from the results of positron annihilation and EXAFS analysis.

2. Experimental

A rod-shaped $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass (Ø 10 mm × 60 mm) was produced by using the tilt casting method in an arc furnace [10,11]. The glass transition temperature T_g and the crystallized temperature T_x of this specimen were 689 K and 781 K, respectively, which were determined by differential scanning calorimetry (DSC) measurement. For positron annihilation measurements and XRD, it was cut into specimens of about 0.5 mm thickness. These specimens were isothermally annealed for 10 h at 673 K (below T_g) and for 2 h at 783 K (above T_x). The as-prepared and annealed specimens were characterized by X-ray diffraction (XRD) measurement.

Positron annihilation lifetime spectra were obtained by using a conventional fast–fast circuit with a time resolution of about 200 ps (FWHM) at room temperature. As a positron source, we used $^{22}NaCl$ with an activity of 286 kBq, which was sandwiched by thin Kapton foils. The positron annihilation lifetime spectrum consists of more than 1.0×10^6 counts. All the positron annihilation lifetime spectra were analyzed by the POSITRONFIT program [12]. Positron annihilation coincidence

* Corresponding author. Tel.: +81 72 254 9812; fax: +81 72 254 9812.
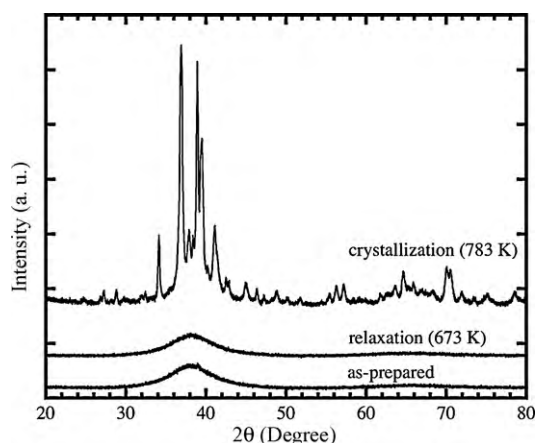E-mail address: horif@mtr.osakafu-u.ac.jp (F. Hori).

Fig. 1. XRD profiles of $Zr_{50}Cu_{40}Al_{10}$ BMGs isothermally annealed for 2 h at 783 K and 673 K. The spectrum for as-prepared specimen is also shown.

Doppler broadening (CDB) measurement was carried out at room temperature. Each CDB spectrum consists of more than 2.0×10^8 counts. The CDB ratio spectrum was obtained by normalizing the momentum distribution of each spectrum to that of Zr or Al metal. It is well established that the change in low electron momentum corresponds mainly to the free volume change, and the detailed profile at higher electron momentum region reflects the local structure and their atomic elements [13].

EXAFS measurements near the Zr K-edge (17.998 keV) were carried out at room temperature at the beam line BL-27B of High Energy Accelerator Research Organization (KEK) synchrotron radiation facility. The values of some parameters (coordination number, average inter-atomic distance and Debye–Waller factor) for the best curve-fitting were decided by using REX-2000 EXAFS analysis code.

3. Results and discussion

3.1. Structural relaxation

XRD spectra of a $Zr_{50}Cu_{40}Al_{10}$ BMG before and after annealing at 673 K for 2 h are presented in Fig. 1. The amorphous state of the specimen is still retained after annealed for 2 h below T_g. In our previous work [6], we reported the good correlation between change in atomic density and the size of open volume measured by positron lifetime technique during annealing in this BMG alloy. Therefore, the open volumes detected by positron techniques can be regarded as well-established free volume [14] in metallic glass. The positron lifetime spectra for this metallic glass could not be decomposed into two or more components. This result shows that there is no pore with large open space in this BMG alloy. Fig. 2 shows the CDB spectrum of Zr50Cu40Al10 BMG, which is annealed for 10 h at 673 K, in
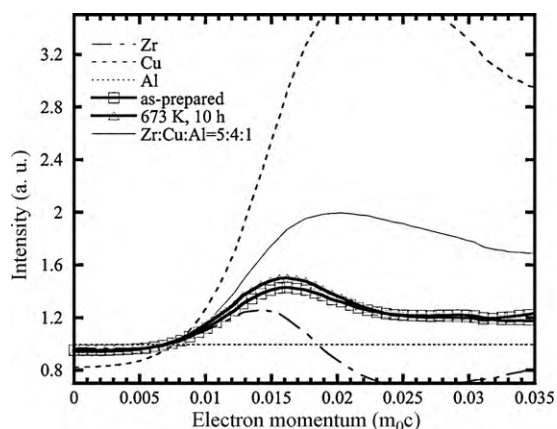

Fig. 2. CDB spectra of as-prepared and isothermally annealed at 673 K $Zr_{50}Cu_{40}Al_{10}$ BMGs, expressed in the form of a ratio of observed CDB intensity to the intensity of pure Al metal.
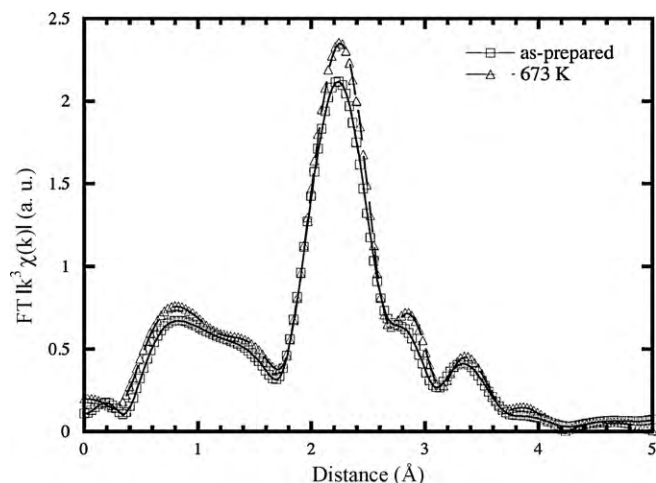

Fig. 3. Fourier transform of Zr K-edge EXAFS spectra for $Zr_{50}Cu_{40}Al_{10}$ BMG as-prepared and annealed at 673 K below T_g.

the form of a ratio to the CDB spectrum of Al metal. For comparison, we also show the CDB spectra of Cu and Zr metals in Fig. 2. These ratio curves provide the chemical fraction around the open volume. If Zr, Cu and Al atoms were homogeneously distributed in the specimen, then we would derive the CDB spectrum shown in Fig. 2 as the solid line (I_{cal}). This ideal spectrum can be calculated by following equation:

$$I_{cal} = a \times I_{Zr} + b \times I_{Cu} + c \times I_{Al} \quad (a + b + c = 1)$$

where I_{Zr}, I_{Cu} and I_{Al} are the positron annihilation Doppler broadening spectrum for pure Zr, Cu and Al, respectively. In this case, we substitute the value $a = 0.5$, $b = 0.4$ and $c = 0.1$ as a chemical composition of this alloy. However, the result of CDB (Fig. 2) shows that the spectrum of experimental result for as-prepared BMG does not match that of calculated spectrum I_{cal}. Besides, observed spectrum is between the spectra of pure Zr and calculated result I_{cal}, showing that the fraction of Zr around free volume is greater than that of composition for alloy system. This result suggests that the fraction of Zr atom around free volume is greater than that of composition for alloy system. As shown in this figure, the isothermal annealing below T_g causes little change in the shape of CDB spectrum, which is in good agreement with our previous work [15]. This result implies that atomic rearrangement around free volume does not take place in this alloy during annealing. On the other hand, the positron lifetime, which corresponds to the size of free volume, decreases by 16 ps after the structural relaxation [6]. These results show that the long-range diffusion around the free volume does not occur and the chemical order of segregated Zr atom around the free volume remains unchanged even during the structural relaxation below T_g.

Fig. 3 shows the normalized experimental Zr K-edge EXAFS spectra obtained by Fourier transform (FT) for as-prepared $Zr_{50}Cu_{40}Al_{10}$ BMG and that thermally annealed for 2 h at 673 K. A main peak appears around 2.2 Å. The FT spectrum of metallic glass is similar to that of other Zr-based metallic glasses including Cu, such as $Zr_{70}Cu_{30}$, $Zr_{70}Cu_{29}Pd_1$ [16] and $Cu_{50}Zr_{50}$ [17]. However, in the case of Zr–Ni based metallic glasses, which do not include any Cu atoms, such as $Zr_{70}Al_{10}Ni_{20}$ and $Zr_{70}Al_9Ni_{20}Pd_1$ [18], the shape of FT spectra is significantly different from that of $Zr_{50}Cu_{40}Al_{10}$ BMG. A similar result has been reported for Zr_2Ni metallic glass at Zr K-edge by Liu et al. [19]. This implies that there are significant differences in coordination configuration between Zr–Cu based and Zr–Ni based metallic glasses. From these facts we suppose that metallic glasses do not have a complete random structure but have some chemical order depending on the alloying system. The FT spectrum of the
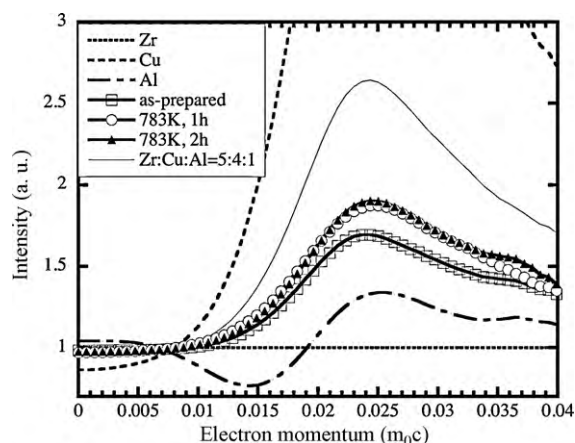
Fig. 4. CDB spectra of as-prepared and isothermally annealed at 783 K $Zr_{50}Cu_{40}Al_{10}$ BMGs, expressed in the form of a ratio of observed CDB intensity to the intensity of pure Zr metal.

Fig. 5. Fourier transform of Zr K-edge EXAFS spectra for $Zr_{50}Cu_{40}Al_{10}$ BMG as-prepared and annealed at 783 K above T_x.

first coordination at 2.2 Å in $Zr_{50}Cu_{40}Al_{10}$ BMG scarcely changes by structural relaxation. It follows from these results that the inter-atomic distance of Zr–Zr and Zr–Cu hardly changes. Though the size of free volume decreases, it is considered that the chemical order of segregated Zr atoms around the free volume does not change during the structural relaxation.

3.2. Crystallization

The XRD spectrum in Fig. 1 clearly shows that the thermal annealing above T_x crystallizes $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass. The similar XRD spectrum for the same alloy system after crystallization has been reported by Zhang et al. [20]. The crystallized specimen shows a reduction in positron lifetime from 164 to 158 ps. This trend of decreasing of positron lifetime by the crystallization is in agreement with the result of Hori et al. [21] and that for $Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$ alloy system by Asoka-Kumar et al. [22]. Fig. 4 shows CDB spectra for as-prepared and crystallized specimens with the spectra for pure Cu and Al metals in the form of a ratio to the CDB spectrum of pure Zr metal. After the thermal annealing above T_x, the peak height of CDB spectrum in electron momentum region around 0.025 m_0c becomes closer to the spectrum for the homogeneous distribution of atoms in accordance with the chemical composition of Zr:Cu:Al = 5:4:1 (solid line in Fig. 4). This result means that the fraction of Zr atoms around the free volume decreases and the segregated Zr atoms around the free volume are dissociated.

Fig. 5 shows the normalized experimental Zr K-edge EXAFS obtained by Fourier transform (FT) for as-prepared $Zr_{50}Cu_{40}Al_{10}$ BMG and annealed one for 2 h at 783 K. From this figure, a new peak around 2.8 Å appears after the crystallization. The temporary analysis of the FT spectrum suggests that the peak around 2.1 Å for the crystallized specimen corresponds to the combination of Zr–Cu and Zr–Zr, and the peak around 2.8 Å corresponds to the combination of Zr–Zr mainly. The change in the position of the peak corresponding to the first coordination indicates that the inter-atomic distance of first coordination slightly shortens. Hence, this peak position change may correspond to the decrease in the size of free volume and the atomic migration around Zr atom.

The second coordination of Zr–Zr atom, which corresponds to the peak around 2.8 Å is formed after the crystallization. The height of this peak is higher than that of the peak at 2.1 Å. This demonstrates that the local structure around Zr atom of crystallized specimen is quite different from that of the relaxed one. From the results of positron annihilation and EXAFS experiments, it is found
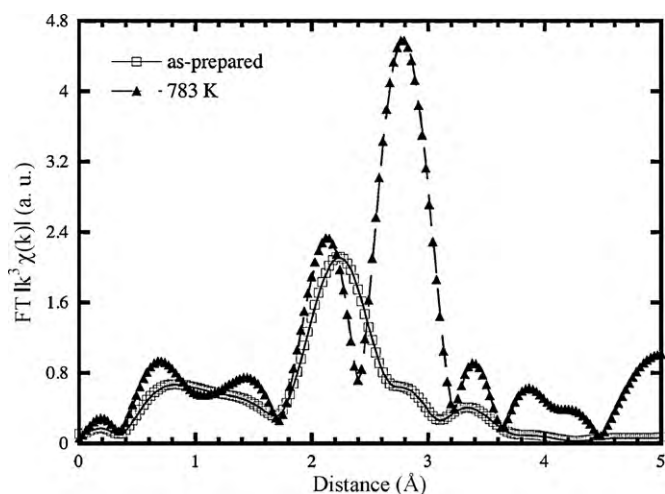
that the chemical order around the free volume is dissociated, and the crystallized order is newly formed during the crystallization. To conclude, the structural relaxation is caused by the shrinkage of the free volume, while the crystallization is ascribed to the shortening of the inter-atomic distance and long-range ordering with disappearance of free volume. As a result, quenched in open volume disappears by crystallization.

4. Conclusions

The relaxation and the crystallization behaviors of $Zr_{50}Cu_{40}Al_{10}$ BMG have been investigated by means of positron annihilation and EXAFS measurements, and the following conclusions have been obtained.

The fraction of Zr atoms around the free volume in $Zr_{50}Cu_{40}Al_{10}$ BMG is greater than 50%, suggesting that ternary $Zr_{50}Cu_{40}Al_{10}$ BMG has the chemical order around the free volume.

During the structural relaxation below T_g, the chemical order around the free volume almost remains unchanged with the decrease in the free volume size. On the other hand, the long-range arrangement around the free volume occurs, and the free volume disappears during the crystallization above T_x.

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