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Free volume in Zr-based bulk glassy alloys studied by positron annihilation techniques

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Abstract. The eutectic $Zr_{50}Cu_{40}Al_{10}$ bulk glassy (BG) alloys, which have a good glass forming ability, have been investigated for various properties, such as toughness, electronic resistivity and so on. Recently, the hypoeutectic $Zr_{60}Cu_{30}Al_{10}$ BG alloys have been paid attention, because they exhibit no degradation of ductility and toughness after the isothermal annealing below the glass transition temperature (T_g). Although the toughness correlates with the free volume to be considered, the free volume of the hypoeutectic BG alloy has not been assessed in detail so far. In order to study the free volume in each BG alloy, therefore, positron annihilation lifetime and coincidence Doppler broadening (CDB) measurements have been performed for $Zr_{60}Cu_{30}Al_{10}$ (hypoeutectic) and $Zr_{55}Cu_{35}Al_{10}$ (middle-composition) and $Zr_{50}Cu_{40}Al_{10}$ (eutectic) BG alloys. The value of the positron lifetime for hypoeutectic BG alloy is virtually the same. Additionally, the CDB ratio curve for hypoeutectic alloy dose not match that for eutectic alloy in an electron momentum region around 0.015 m_0c, indicating that the fraction of Zr atoms around the free volume in hypoeutectic BG alloy is greater than that in eutectic BG alloy. Moreover, the CDB results show that the local structure around free volume for hypoeutectic BG alloy is different from that for eutectic BG alloy.

1. Introduction

Zr-based bulk glassy alloys show high tensile strength [1] and a high Chrapy impact value [2]. These alloys are recognized by good balance between high strength and high toughness. However, Zr-based BG alloys often show the degradation of mechanical properties owing to structural relaxation. Recently, our co-workers have reported that the fatigue behaviour of hypoeutectic $Zr_{60}Cu_{30}Al_{10}$ BG alloys remains unchanged after complete structural relaxation [3]. The free volume is defined as frozen excess open volume in the glassy alloys and perceived as an important factor to describe some properties for glassy alloys. Hence, the fatigue behaviour of BG alloys is also associated with free volume. However, the evaluation based on microscopic measurement of free volume for hypoeutectic BG alloys has not been carried out, so that the relation between free volume and mechanical properties has not been clarified yet. Positron annihilation lifetime can detect and estimate the size of free volume, and positron annihilation coincidence Doppler broadening (CDB) measurement provides the information on the detailed electron distribution around the free volume. Therefore, the local atomic element analysis around free volume has become possible by this technique. So far, we have reported that there is a lot of Zr fraction around free volume for eutectic BG alloy [4]. In this study, we evaluate and discuss the size of free volume and its structure for ternary eutectic, hypoeutectic and other composition of Zr-Cu-Al BG alloys by using positron annihilation techniques. We also estimate the relationship between macroscopic change in density and microscopic change in free volume size during structural relaxation for eutectic BG alloys.

2. Experimental

As a starting material for bulk glassy alloys, ternary eutectic $Zr_{50}Cu_{40}Al_{10}$ (E-BG), hypoeutectic $Zr_{60}Cu_{30}Al_{10}$ (H-BG) and another composition (middle-content of zirconium) $Zr_{55}Cu_{35}Al_{10}$ (M-BG) alloy ingots were prepared by arc melting the mixtures of pure Zr, Cu and Al metals in an argon gas atmosphere. To avoid oxygen contamination, a special crystalline Zr rod (<100 mass ppm oxygen) was used. The master alloy was completely re-melted and cast into a rod shaped cast vessel (ϕ8 mm x 60 mm), which is called the tilt casting method. E-BG alloy specimens were annealed isothermally for 5 hours at 473, 573 and 673 K below glass transition temperature (T_g). The phase characterization of the as-prepared and annealed samples was performed by X-ray diffraction (XRD) measurements. The density of the cast Zr-Cu-Al BG alloys was measured by Archimedes method [5] at room temperature. Positron annihilation lifetime spectra were measured by using a conventional fast-fast circuit with a time resolution of about 200 psec (FWHM) and slow positron beam at Japan Atomic Energy Agency (JAEA) at room temperature. As a positron source for conventional method, we used ^{22}NaCl with an activity of 286 kBq, which was sandwiched by thin Kapton foils. The energies of the positron beams were set to 15 keV. The positron annihilation lifetime spectra consist of 1.0 x 10^6 counts. All the positron annihilation lifetime spectra were analyzed by the POSITRONFIT program [6]. Positron annihilation coincidence Doppler broadening (CDB) measurement was carried out at room temperature. Each CDB spectrum consists of more than 1.0×10^8 counts. The CDB ratio spectrum was obtained by normalizing the momentum distribution of each spectrum to that of 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 [7].

3. Results and discussions

Figure 1 shows the results of positron annihilation lifetime and density for E-BG, H-BG and M-BG alloy. The values of positron lifetime for these alloys are nearly constant. We tried all positron lifetime spectra to decompose into two or more components, but only one component was analyzed in all samples. Generally, positron lifetime value provides the information about not only the open volume size of vacancy type defect but also its concentration. Therefore, this result shows that the same size of free volume exists in these alloys. Moreover, the result of density measurement does not correspond to that of positron lifetime. Atomic density for each alloy is not constant but depends on Zr atom content. This difference between density and positron lifetime results may be caused by the variation of free volume concentration for each alloy. This is considered that the melting temperature of Zr based BG alloy varies with Zr content, so that the amount of quenched in free volume of these alloys becomes different. Then, we estimate the local structure especially focus on Zr atom fraction around the free volume for each BG alloy from the results of CDB ratio analysis.

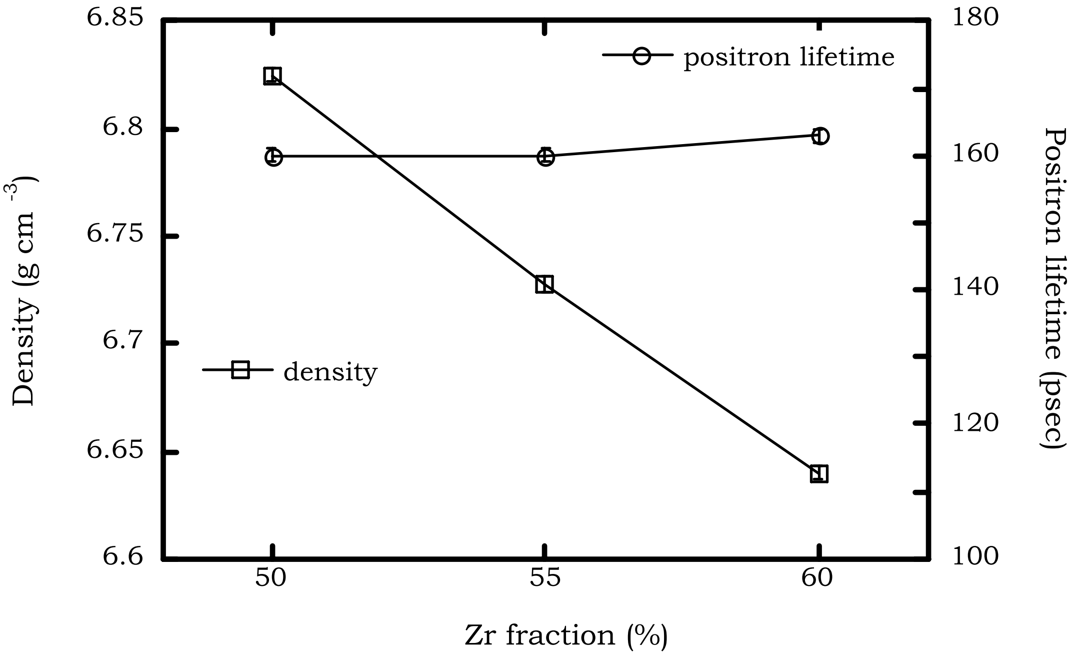

Figure 1. Positron annihilation lifetime and bulk density for ternary E-BG, H-BG and M-BG alloys.

Figure 2 shows CDB ratio curve of each BG alloy with those of Cu and Zr metals, expressed as a ratio of CDB intensity of Al. The positron affinities of A_+ for Zr, Cu and Al are -3.98, -4.81 and -4.41 eV, respectively [8]. It seems that all elements might be attracted to positron because the differences of the positron affinity ΔA_+ between A_+^{Al}, A_+^{Cu} and A_+^{Zr} are not so big. Even if Zr precipitates exist in this alloy matrix, positron may not detect them because positron affinity for Zr is lower than that for other elemental atom (Al and Cu). This result indicates that positron is not necessarily selectively annihilated with Zr atom. Nevertheless, CDB ratio curve shows a characteristic feature of Zr atom. This fact suggests that Zr atoms tend to aggregate around free volume in this system of glassy alloy. Moreover, it can be recognized from this figure that the electron momentum distribution profiles for these BG alloys depend on chemical composition. The CDB spectra indicate a marked difference between E-BG and H-BG alloy in the region of the peak around 0.015 m_0c. In other words, the spectrum of the H-BG alloy is more similar to that of Zr metal than that of the E-BG alloy. This result exhibits that the fraction of Zr atoms around free volume in H-BG and M-BG alloy is greater than that in E-BG alloy. This fact reveals that the local structure around free volume for Zr-Cu-Al ternary BG alloys strongly depends on their chemical composition. This difference of local structure may be related to the property change of brittleness for Zr-Cu-Al BG alloys [3].

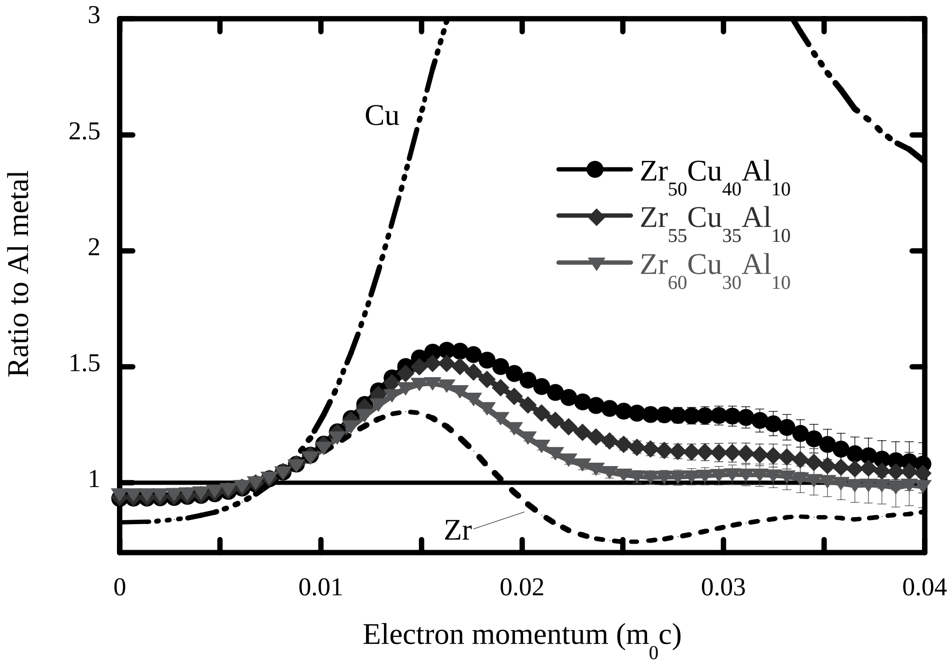

Figure 2. CDB ratio spectra of E-BG, M-BG, and H-BG alloy with those of Cu and Zr metals, expressed as a ratio of CDB intensity of Al metal.

Figure 3 shows each changing value of bulk density and positron lifetime measured by using positron from radio active source 22-Na and slow positron beam with energy of 15 keV for E-BG alloy after each isothermal annealing at 473, 573 and 673 K for 5 hours. As shown in this figure, the difference of positron lifetime comparing with as-prepared sample increases with increasing annealing temperature. This result agrees with our previous results [4,9,10]. As can be seen from this figure, density increases, and absolute value of positron lifetime decreases with increasing annealing temperature. This result means that density increases caused by the shrinkage of free volume, depending on annealing temperature.

As mentioned above, the size of free volume for each as quenched BG alloy is virtually the same, although their density depends on the Zr fraction of alloy composition. Further, Zr atom fraction around free volume, namely the local structure near by the free volume, for these alloys is essentially different from each other. Hence, it can be supposed that the relaxation process of local structure and macroscopic change of density for each alloy during annealing are not always analogous. In this point of view, other relaxation measurements for a series of chemical composition and annealing temperature are needed.

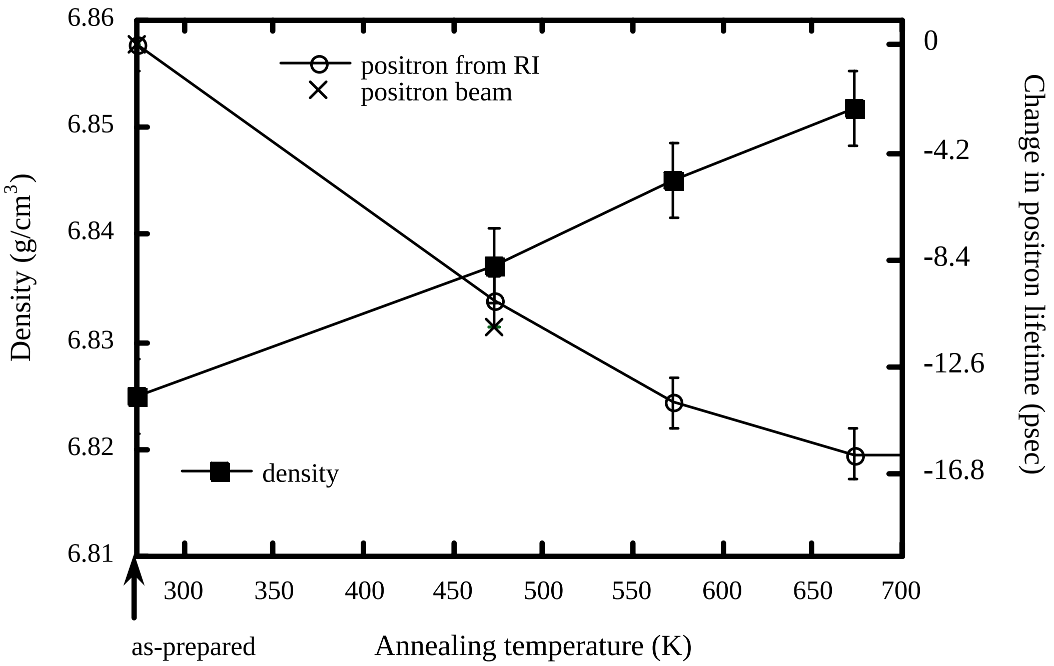

Figure 3. Change in positron lifetime measured by using positron from RI and slow positron beam and bulk density of E-BG after isothermal annealing at 473, 573 and 673 K for 5 hours.

4. Summary

The nature of free volume for various compositional Zr-Cu-Al ternary bulk glassy alloys has been studied by positron annihilation lifetime and coincidence Doppler broadening measurements, and we obtained following conclusions.

The size of free volume for Zr-Cu-Al ternaly bulk glassy alloys is essentially the same without depending on their chemical composition. The number density of free volume, which might be corresponding to bulk density, depends on alloy composition. It found that the local structure around free volume for hypoeutectic bulk glassy alloys is different from that for other composition of bulk glassy alloys. Moreover, free volume change especially around free volume after relaxation corresponds to change in density for eutectic alloy.

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