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Study of local structure in hyper-eutectic Zr-Cu-Al bulk glassy alloys by positron annihilation techniques

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Abstract. The Zr-Cu-Al bulk glassy (BG) alloy, which has amorphous structure, possesses various properties such as high strength and toughness with compositional dependence. In the present study, density, positron annihilation lifetime and coincidence Doppler Broadening measurement have been performed for various compositional hyper-eutectic Zr-Cu-Al BG alloys. The density of hyper-eutectic Zr-Cu-Al BG alloys increases with decreasing of Zr fraction. In contrast, positron lifetime for all compositional alloys is almost constant about 165 psec. In addition, the CDB ratio profile is almost the same for hyper-eutectic alloys. This unchanging trend of CDB ratio profile is quite different from that of hypo-eutectic BG alloys. These results reveal that different internal structure exists in hyper and hypo-eutectic BG alloys.

1. Introduction

Zr-Based bulk glassy alloy have attracted a great deal of attention over the past several years due to a high strength and a high toughness [1]. Recently, it was reported that the model for the glass forming ability is based on phase selection of the glass [2][3]. In addition, our co-workers have reported that the difference of the thermal volume coefficient and melting point the various compositions of Zr-based BG alloys [4]. Compositional dependence of these characteristics has been considered caused by the difference of the local structure such as clusters. Because those show tendencies of the change are different in the hypoeutectic and hypereutectic, it is considered that the local structure is different in the hypoeutectic and hypereutectic. Besides, the bulk glassy alloys have the free volume defined as frozen open volume and are not completely random structure, but forming clusters of short-range orderings and random areas [5]. So far, we have reported that there are a lot of Zr atoms around the free volume [6]. In the present study, it is reported that the evaluation based on microscopic structure measurement of the free volume for eutectic and hypoeutectic Zr-based bulk glassy alloy. However, the evaluation based on the free volume for hypereutectic have not been clarified yet. In this study, through the comparison with hypo-eutectic BG alloy, we studied the local structure around free volume in hyper-eutectic Zr-Cu-Al BG alloys by density measurement and positron annihilation techniques, such as positron annihilation lifetime and coincidence Doppler broadening (CDB) measurements. Positron lifetime is method for evaluating the electron density in free volume, and coincidence Doppler broadening measurement provides the information on the detailed electron distributions around free volume. In addition, in order to evaluate quantitatively, we calculated the S-parameter and W-parameter for the alloy composition from CDB spectra.

2. Experiments

The rod-shaped glassy alloys of hypo-eutectic $Zr_XCu_{90-X}Al_{10}$ (X=65, 60, 55), eutectic $Zr_{50}Cu_{40}Al_{10}$ and hypo-eutectic $Zr_XCu_{90-X}Al_{10}$ (X=49, 48, 47, 46, 45) were prepared by the tilt casting method in the arc furnace [7]. For positron annihilation measurements, these samples were cut into specimens with about 0.4 mm thickness. The as-prepared specimens were characterized by X-ray diffraction (XRD) measurements. In addition, we examined the glass transition temperature (T_g) and crystallization temperature (T_x) by differential scanning calorimetry (DSC), in order to confirm they are glass or not. The densities of these samples were also measured by Archimedes method at room temperature [8]. Positron lifetime and coincidence Doppler broadening (CDB) measurement have done for all specimens at room temperature. The positron annihilation lifetime spectra consist of 1.0×10^6 counts. All the positron annihilation lifetime spectra has analyzed by the RESOLUTION program. Each CDB spectra consists of more than 1.0×10^8 counts. The CDB ratio spectrums were 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 [9]. CDB spectra were characterized by S and W parameters. The S and W parameters were determined as the ratio of the γ-ray counts in the range of $|P_L|\leqq3.7\times10^{-3}$ m_0c and $1.1\times10^{-2}\leqq|P_L|\leqq1.7\times10^{-2}$ m_0c, respectively.

3. Results and discussion

Figure 1 shows the density for hyper-eutectic, hypo-eutectic and eutectic BG alloy. In this figure, the density linearly decreases with increasing Zr fraction. This systematic change with Zr fraction seems to be owing to total atomic density. That is, there is no different changing in macroscopic structure with Zr fraction. Figure 2 shows the results of positron annihilation lifetime measurement for all alloy composition BG alloy. The positron lifetime of eutectic and hypo-eutectic BG alloy agree with our previous reports [10, 11]. In this figure, positron lifetime remains stable for Zr fraction. Generally, it is well known that lifetime corresponds to the free volume size, such as vacancy [9]. It is considered that the free volume size in these alloys remains stable for Zr fraction.

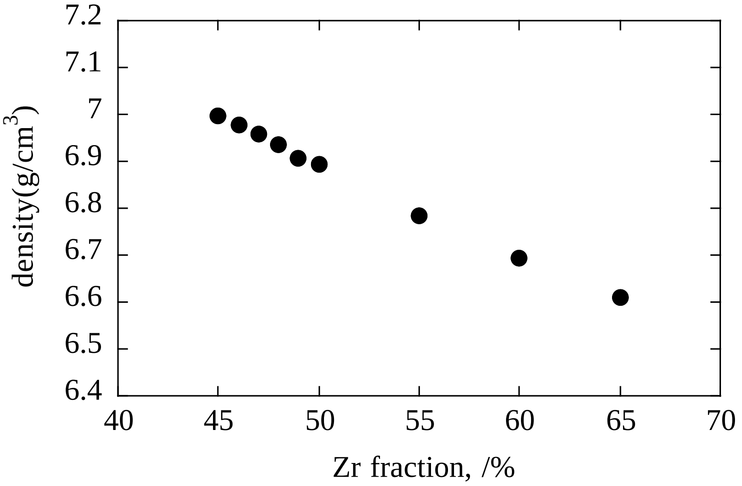

Figure 1. Density of Zr-Cu-Al bulk glassy alloys as a function of Zr fraction.

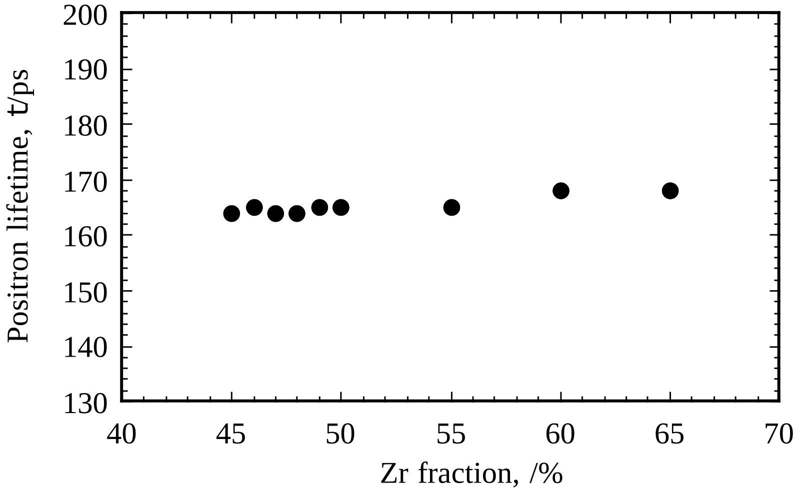

Figure 2. Positron annihilation lifetime of Zr-Cu-Al BG alloys as a function of Zr fraction.

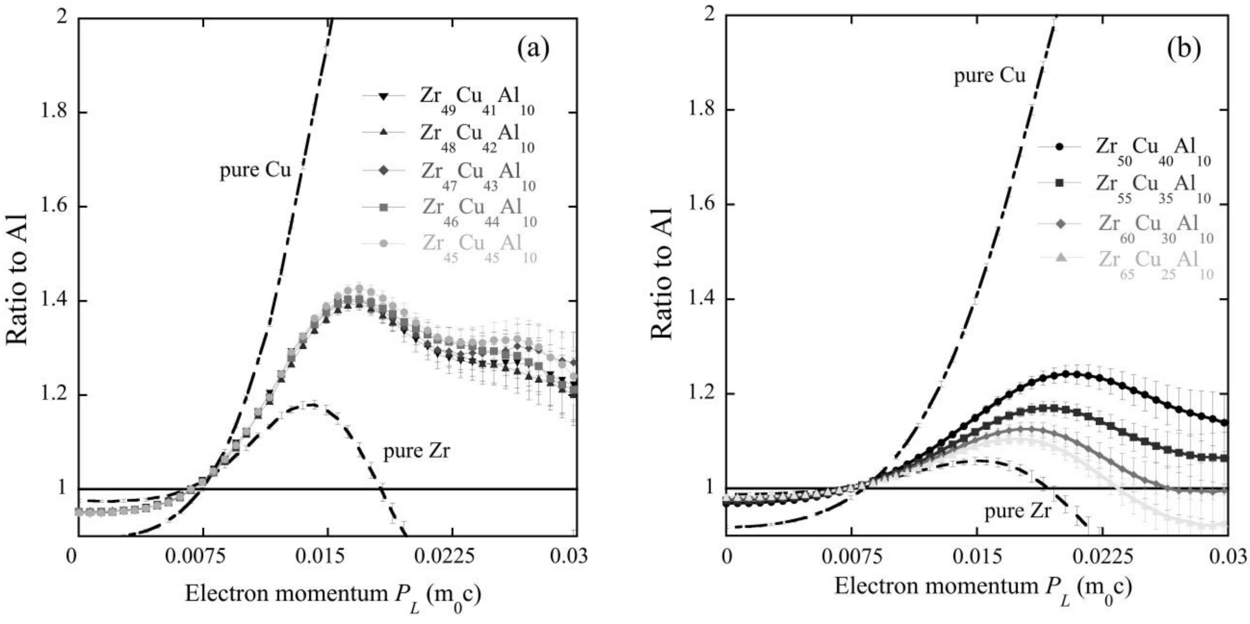

Figure 3. CDB ratio spectra of (a) hyper-eutectic and (b) hypo-eutectic bulk glassy alloy with those of Cu and Zr metals, expressed as a CDB ratio intensity of Al metal.

Figure 3 (a) and (b) shows the ratio spectra of CDB for all BG alloy with those of Cu and Zr metals, expressed as a ratio of CDB intensity of Al. The ratio profiles normalized by the CDB spectrum of pure Al are most clear in detail other than that of Fe and Zr. Also, only the broadening of ratio spectra for pure Zr in figure 3(a) and (b) is not consistent seemingly each other. This difference comes from the energy resolution difference by different measurement period, so that this difference has not influence to our discussions. In figure 3(a), the ratio spectra of hyper-eutectic alloys have little change with Zr fraction. In contrast, in case of the ratio spectra of hypo-eutectic alloys, systematically change is confirmed as shown in figure 3(b). With increasing Zr fraction, these ratio spectra approach to the ratio spectrum of pure Zr. This changing trend agrees well with our previous study [11]. It has reported that the icosahedral cluster is present around free volume in Zr-based BG alloys [11, 12]. Therefore, it is considered that the ratio of Zr atom around free volume increases with increasing Zr fraction. Both S-parameter and W-parameter as a function of Zr fraction for hyper-eutectic and hypo-eutectic BG alloys are shown in figure 4(a) and (b). In figure 3, the characteristic peak appears in high electron momentum around 0.015m_0c, we selected this range as W-parameter. As seen in figure 4(a), S and W parameters for hyper-eutectic BG alloys are almost constant for Zr fraction, showing that the atomic element ratio around free volume does not change. In contrast, W-parameters in hypo-eutectic BG alloys change with Zr fraction as shown in figure 4(b). Comparing the results for hyper-eutectic and hypo-eutectic BG alloys, the changing trend of atomic element ratio is clearly different. This result can be considered as follows; that is the local ordered structure around free volume in hyper-eutectic BG alloys does not change even though Zr fraction increases. On the other hand, this local structure systematically changes with Zr fraction for hypo-eutectic BG alloys. This result is not consistent with the result of positron lifetime measurement. That is, the positron lifetime remains constant for Zr fraction, but W parameter changes only in case of hypo-eutectic BG alloys. This result can be supposed that the size of free volume becomes larger and surrounding Zr atom ratio increases around free volume with increasing of Zr fraction. Consequently, total electron density does not change at a free volume site in hypo-eutectic composition region.

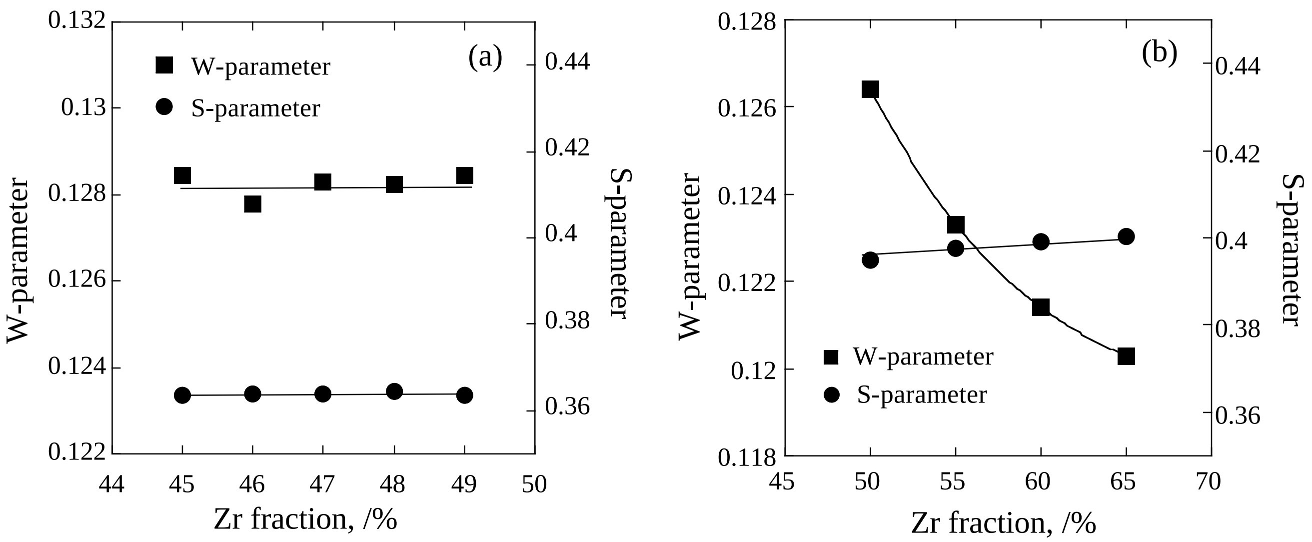

Figure 4. Each W-parameters and S-parameters of (a) hyper-eutectic and (b) hypo-eutectic bulk glassy alloy.

4. Summary

The difference of local structure for hyper-eutectic and hypo-eutectic Zr-Cu-Al bulk glassy alloys has been studied by positron annihilation lifetime and coincidence Doppler broadening measurements, and we obtained following conclusions. Regardless of the hyper-eutectic and hypo-eutectic, the density changes systematically with Zr fraction. On the other hand, the local structure around free volume in hyper-eutectic bulk glassy alloys has different trend from that in the hypo-eutectic one. The local structure around free volume for hyper-eutectic Zr-Cu-Al bulk glassy alloys is stable irrespective of hypo-eutectic Zr-Cu-Al bulk glassy alloys.

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