Free volume change in Zr$_{50}$Cu$_{40}$Al$_{10}$ glassy alloy by the annealing studied by positron annihilation spectroscopy

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Abstract. It is well known that structural relaxation in a bulk metallic glass affects some properties such as viscosity, electrical conductivity, and ductility. The free volume in glassy alloy, which is open volume retained by rapidly solidification from liquid state, has a significant roll for those properties. In order to discuss the nature of free volume in a Zr$_{50}$Cu$_{40}$Al$_{10}$ bulk metallic glass, positron lifetime measurements have been performed for this metallic glass before and after annealing, and all positron lifetime spectra have been decomposed into multi components as a size distribution function by use of CONTIN-PALS II program. The positron lifetime distribution for this metallic glass has a broad spectrum comparing to crystal metal including a single vacancy, and its average lifetime corresponds to the free volume size. This width of positron lifetime (free volume size) distribution decreases by the annealing at 673 K. This change of the positron lifetime distribution can be attributed to a free volume relaxation.

1. Introduction

Bulk metallic glasses (BMGs) have advanced properties, including high specific strength, good corrosion resistance and large elastic strain limits [1]. The metastable and disordered state of metallic glass raises some questions about thermal stability. Frozen excess open volume in the metallic glass has been perceived as an important factor to describe some properties for metallic glasses under the thermal activation process in some temperature ranges: below glass transition temperature ($T_g$), above $T_g$ and above crystallization temperature ($T_x$) according to relaxation theory in metallic glasses [2]. However, not all studies to date have revealed the nature of the free volume directly. So far, we have investigated the free volume relaxation process in Zr$_{50}$Cu$_{40}$Al$_{10}$ ternary system of bulk metallic glass below $T_g$ using positron annihilation techniques, which can detect and estimate the size of free volume [3]. In that study, we have reported that the free volume relaxation process depending on temperature directly reflects to changes in density. Recently, C. Nagel et al. have demonstrated through positron annihilation measurements that the free volume relaxation process far below $T_g$ in the Johnson glass (Zr$_{46.7}$Ti$_{8.3}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$) does not need high activation energy to promote the evolution to more stable amorphous state [4].

In the free volume theory, free volume in amorphous materials is assumed as the hole derived from density fluctuation of element [5]. On the other hand, recently, some groups suggest that quasicrystal
like local clusters exist in some metallic glasses; icosahedral type of clusters exist in Zr-based metallic glasses [6], and trigonal prism-like structural clusters exist in Fe-based metallic glasses [7]. These studies imply that it is difficult for the simple “hole type” free volume model to describe the nature of free volume. Furthermore, our results demonstrate that the long range diffusion does not occur during relaxation, suggesting the possibility of internal cluster relaxation [3]. Accordingly, development of the free volume model is becoming important.

In this work, we discuss the nature of free volume and the size distribution of free volume from the viewpoint of positron annihilation and estimate change in the distribution after relaxation below $T_g$.

2. Experimental
A rod-shaped sample of Zr$_{50}$Cu$_{40}$Al$_{10}$ bulk metallic glasses ($\phi$ 8 mm × 60 mm) was produced by the tilt casting method in an arc furnace [8,9]. The glass transition temperature of this sample was 675 K, which was determined by differential scanning calorimetry (DSC) measurement. For positron annihilation measurements, this sample was cut into specimens of about 0.5 mm thickness. These specimens were annealed isothermally at 673 K up to 36000 s. The as-prepared and annealed specimens were characterized by X-ray diffraction (XRD) measurements.

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. In order to derive fully accurate spectra, a digital stabilizer of SEIKO EG&G was used. 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 spectra consist of more than $3.0 \times 10^6$ counts. All the positron annihilation lifetime spectra were analyzed by the POSITRONFIT program [10] and the CONTIN-PALS II program [11,12] which execute the continuous lifetime distribution analysis. The CONTIN program provides the annihilation probability density function $f(\lambda)$. The continuous probability density function $f(\lambda)$ is gained by deconvolution of the experimental lifetime spectra using a Laplace inversion technique [11,12]. Positron annihilation coincidence Doppler broadening (CDB) measurements were carried at room temperature. Each CDB spectrum consists of more than $10^9$ counts.

3. Results and Discussion
XRD profiles of as-prepared and isothermally annealed Zr$_{50}$Cu$_{40}$Al$_{10}$ bulk metallic glass sample at 673 K for 10 h are shown in figure 1. This result reveals that the amorphous state of this sample was retained even after long time annealing just below $T_g$.

![Figure 1. XRD profiles of as-prepared and 10 hours annealed at 673 K for Zr$_{50}$Cu$_{40}$Al$_{10}$ bulk metallic glass.](image-url)
Figure 2 shows CDB spectrum of relaxed Zr_{50}Cu_{40}Al_{10} bulk metallic glass expressed in the form of ratio to that of Al metal. For comparison, we also show the CDB ratio curves of Cu and Zr to Al. It can be recognized from this figure that the electron momentum distribution profile after relaxation is essentially the same as that of as-prepared specimen, although it was observed that low electron momentum region (0-0.006 \( m_0c \)) decreases with increases of inner part of momentum distribution (about 0.015 \( m_0c \)) only reflecting the change in free volume size. This result implies that long range diffusion or drastic rearrangement do not occur by long time annealing below \( T_g \), while the free volume decreases and the bulk density clearly increases [13].

On the other hand, figure 3 shows the change of the positron annihilation probability density distribution \( f(t) \) between as-prepared and annealed samples of Zr_{50}Cu_{40}Al_{10} bulk metallic glasses. This result indicates the size of free volume in this glassy alloy has a broad distribution. The mean positron lifetime of the as-prepared sample analyzed by POSITRONFIT program is about 163 ps. This value agrees with that of our previous work [3].

Table 1. Positron lifetimes in ZrCuAl bulk metallic glass and other experimental value of pure metals.

| Zr_{50}Cu_{40}Al_{10} bulk metallic glass | Zr   | Cu   | Al   |
|----------------------------------------|------|------|------|
| as-prepared                            | 163  | 147  | 155  |
| 673 K                                   |      |      |      |
| 473 K                                   | 165  | 110  | 163  |
|                                        | [3]  | [14] | [14] |

According to the free volume model suggested by Cohen and Turnbull [5], a free volume in amorphous materials is presumed as the “hole” derived from density fluctuation of element. Assuming the existence of two or more annihilation states in amorphous, one is defect type open volume and other is defect free matrix, it is thought that two or more peaks in the positron distribution function
should appear. In this case, however, only one peak was observed. This means that the large amount of free volume exists, or disordered and broaden atomic distances have distribution in this sample.

![Figure 3](image)

**Figure 3.** The probabilities of annihilation site $f(t)$ are plotted as a function of positron lifetime, $t$, for as-prepared and isothermally annealed Zr$_{50}$Cu$_{40}$Al$_{10}$ bulk metallic glass.

Secondly, structural relaxation by the annealing below $T_g$ leads the positron lifetime distribution shift to lower value. The decrease of the peak value, which is about 12 ps, was derived by the analysis of the positron lifetime distribution function. This lifetime change approximately agrees with the mean lifetime change derived by two state trapping analysis (POSITRONFIT). Moreover, the width of distribution function for relaxed sample becomes narrow, mainly on the large size part of free volumes, comparing to that for the as-quenched sample. These results suggest that annealing out of free volume of larger size will takes place preferentially.

4. Conclusions
Distribution of free volume in the Zr$_{50}$Cu$_{40}$Al$_{10}$ bulk metallic glass during relaxation below $T_g$ has been studied by positron annihilation lifetime analyzed by positron continue lifetime function and coincidence Doppler broadening techniques, and the following conclusions have been obtained.

It can be recognized from the result of CDB spectra that the electron momentum distribution profile after relaxation is essentially the same as that of as-prepared specimen. This result implies that the long range diffusion or the drastic rearrangement around free volume do not occur during relaxation.

The size of free volume quenched in bulk metallic glass has a broad distribution with only one main peak.

It was found that the width of positron lifetime distribution function, of which reflects the free volume size distribution for relaxed sample, is narrower than that for as-quenched one. This relaxation of free volume takes place mainly in the part of large size free volume.

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