Behavior of free volume in ZrCuAl bulk metallic glass after irradiation

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Abstract. Free volumes in Zr₅₀Cu₄₀Al₁₀ bulk metallic glasses irradiated by 100 MeV and 200 MeV Xe ions and 2 MeV electrons at room temperature have been investigated by using positron annihilation techniques, the micro Vickers hardness and X-ray diffraction measurements. No crystallization took place due to both ion and electron irradiations. The coincidence Doppler broadening spectra of annihilation gamma rays also remained unchanged by ion and electron irradiation. Meanwhile, an increase and a decrease of positron lifetimes after electron and ion irradiation, respectively, were observed. This suggests the structural modification of free volumes. The response of positron lifetime to ion and electron irradiations may be connected with the tendency of hardness.

1. Introduction

The bulk metallic glasses (BMGs) are expected to be useful for various applications due to their superior mechanical properties, hardness, strength, corrosion resistance and micro-formability [1-3]. We suggest that the properties of BMGs are further improved by irradiation. So far, thin film of metallic glass with electron and ion irradiation has been extensively studied [4-8]. Thin film metallic glasses are crystallized due to both electron [4] and ion irradiations [7-8]. However, we suspect that different irradiation indoses may appear for BMGs because of indose of thickness. In this study, we investigated the effects of ion and electron irradiations on the free volumes and mechanical properties of ZrCuAl BMGs.

2. Experimental procedure

The samples (Ø 8 mm x 0.5 mm discs) were cut from a Zr₅₀Cu₄₀Al₁₀ BMGs (Ø 8 mm x 60 mm) rod fabricated by the tilt casting method in an arc furnace [9] and polished to mirror surfaces. These were irradiated by 100 MeV or 200 MeV Xe ions with a maximum dose of about 1.0 x 10¹⁴ ions/cm² or 2 MeV electrons with a maximum dose of about 1.4 x 10¹⁸ e⁻/cm² at room temperature. Using a ²²NaCl source (172 kBq) deposited on thin Kapton foils, positron annihilation lifetime (PAL) and coincidence Doppler broadening (CDB) measurements were carried out at room temperature. All the PAL spectra were analyzed by RESOLUTION program [10]. To confirm crystallinitities of the samples due to
irradiation, X-ray diffraction (XRD) measurements were performed using a Rigaku Ultima IV. Furthermore, micro-Vickers hardness test was performed before and after irradiation by using a Shimadzu HMV-2 with applied load of 200 and 1000 g imposed for 10 s.

3. Results and discussion

3.1. Free volume

Figure 1 shows the XRD patterns obtained for the as-prepared sample, the samples irradiated with 2 MeV electrons, 100 MeV and 200 MeV Xe ions and the sample annealed at 773 K without irradiation. The broad peak observed for the as-prepared sample indicates its amorphous state. After the heat treatment at 773 K, the peak becomes sharp suggesting the occurrence of crystallization. Similar results have been reported by Matsubara et al. [11]. The peak widths observed after electron and ion irradiations are nearly the same as that of the as-prepared sample. This indicates that the crystallization does not take place due to the above irradiations.

Figure 2 shows the positron lifetimes obtained after 2 MeV electron irradiation, 100 MeV and 200 MeV Xe ion irradiations as a function of dose. All the positron lifetime spectra were analyzed considering one lifetime component. The positron lifetime increases after electron irradiation. This indicates that the size of free volumes becomes large by electron irradiation. On the other hand, the positron lifetime decreases after Xe ion irradiation. The decrease of positron lifetime is more significant for 200 MeV Xe ion irradiation at the dose of $10^{14}$ ions/cm$^2$. Hori et al. have reported that the decrease of positron lifetime observed upon annealing is caused by the reduction of free volume size associated with the structural relaxation and crystallization [12-13]. The decrease of positron lifetime after Xe ion irradiation may be explained in the similar way to it. Also, higher energy irradiation causes more shrinking of free volume.

Figure 3 shows the CDB spectra (ratio to that of pure Al) obtained for the as-prepared sample, the samples irradiated by 2 MeV electrons and 200 MeV Xe ions. For comparison, the CDB spectra for pure Zr and pure Cu are also plotted. The CDB spectrum of the as-prepared sample does not match the spectra of Zr, Cu and Al. This means that free volumes, where positrons are localized, are not surrounded by one specific element. Ishii et al. found the segregation of Zr atoms around free volumes in the same BMG alloy sample [14]. That is, the fraction of Zr atoms around free volumes is greater than that of chemical composition for this alloy system. There are no significant changes in the CDB spectra at any irradiation conditions. Namely, the elemental ratio around free volumes, where positrons are localized, does not change by irradiation.

![Figure 1. XRD patterns of the Zr$_{50}$Cu$_{40}$Al$_{10}$ BMGs in the as-prepared state, after 2MeV electron, 100 MeV and 200MeV Xe ion irradiations and after the heat treatment at 773 K.](image-url)
Taking into account of the above results, it is concluded that electron irradiation enhance the free volume size without atomic reconstruction in Zr$_{50}$Cu$_{40}$Al$_{10}$ BMGs. Similar behavior due to structural relaxation by heat treatment was observed below the glass transition temperature [12]. While, ion irradiation reduces the free volume size without atomic reconstruction. The reduction of free volumes with atomic ordering due to crystallization were found above the glass transition temperature [13]. Therefore, it is considered that crystallization does not occur in Zr$_{50}$Cu$_{40}$Al$_{10}$ BMGs by electron and Xe ion irradiation.

Figure 3. The CDB (ratio to that of pure Al spectrum) spectra of the samples irradiated with (a) 2MeV electrons and (b) 200 MeV Xe ions. In both figures, the CDB spectra of the as-prepared sample, pure Cu and Al metals are also plotted.
Figure 4. The Vickers micro-hardness obtained after (a) 2 MeV electron irradiation and (b)100 MeV and 200 MeV Xe irradiations as a function of irradiation dose.

3.2. Hardness

Figure 4 shows the Vickers micro-hardness (HV) measured after electron and Xe ion irradiation. The hardness of Zr50Cu40Al10 BMG is changed by electron and ion irradiation. The micro-hardness increases by electron irradiation, and it decreases by Xe ion irradiation. These features seem to be qualitatively in good agreement with the change of free volume size shown in Fig. 2. Iqbal et al. reported that the increase of hardness of Zr55Cu30Al10Ni5 BMG by heat treatment may be related to the formation of crystalline phase [16]. Yokoyama et al. reported that the hardness of this alloy does not change by annealing below the glass transition temperature [15]. Consequently, it can be supposed that the change of hardness by ion irradiation is not caused by structural relaxation. However, the hardened mechanism by the electron irradiation is difficult to explain. In order to clarify the mechanism of hardness change by irradiation, the further experiments and analyses are still needed.

4. Conclusions

In this study, the structural changes of Zr50Cu40Al10 BMG after electron and swift heavy ion irradiation were studied by employing the positron annihilation spectroscopy, the XRD and the hardness measurements. No crystallization after electron and Xe ion irradiations was observed, while the different structural changes were induced by electron and Xe ion irradiation. That is, the free volume size in BMG increases after electron irradiation and decreases after Xe ion irradiation without compositional changes. These features are compatible to the changes of hardness upon irradiation. Our results suggest that swift heavy ion irradiation results in more important structural modifications to the “bulk” metallic glass as compared to the electron irradiation.

The absence of crystallization upon irradiation is contradictory to the previous reports concerning the crystallization of thin film metallic glasses by irradiation [4, 7-8]. We suppose that the radiation effect for metallic glass strongly depends on the thickness and also incident ion energy. For instance, crystallization of Zr55Cu30Al10Ni5 BMG by 10 keV Ar ion irradiation with total dose of 2.7x10\(^17\) ions has been reported [16]. The further studies are still needed to elucidate the effects of sample thickness and irradiation condition on the modification of metallic glasses.

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