Positron annihilation study of free volume in electron irradiated $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloy: Effects of thermal relaxation before irradiation

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Abstract. Change in free volume reflects various properties such as hardness and ductility of glassy alloys. The electron- and ion- irradiations affect the free volume of ZrCuAl bulk glassy alloys that is associated with the mechanical properties. In this study, as-quenched $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys and structural relaxed one by annealing for 5 hours at 673K below glass transition temperature (T_g) were irradiated by 8 MeV electrons with a maximum fluence of about 2×10^{18} e^-/cm^2 at room temperature. The behaviour of free volume in these samples was investigated by positron annihilation techniques. X-ray diffraction measurements showed that no crystallization occurred after the irradiation. We observed the positron lifetime increased by the irradiation for both as-quenched and structural relaxed samples. The increases in positron lifetime at 2×10^{18} e^-/cm^2 were 9 psec for as-quenched and 12 psec for relaxed sample, respectively. In addition, the increase in positron lifetime with irradiation fluence was clearly different for the two types of sample. These facts imply that the thermal relaxation before irradiation of $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloy influences the radiation effects, especially the free volume change.

1. Introduction

The Zr-based bulk glassy alloys are known to have a good glass forming ability, and attractive mechanical properties such as high strength and toughness [1]. These properties closely related to change in "free volume", which means frozen excess open volume containing in glassy structure [2]. The bulk glassy alloy has superior stabilized structure, while it is nonequilibrium state. On the other hand, various approaches have been studied to improve the poor ductility of these metallic glasses. One of the most popular is to anneal them. It is well known that annealing below glass transition temperature (T_g) results in "structural relaxation", with an increase in density, but without crystallization [2]. This structural relaxation has relation with the shrinkage of free volume [8]. According to recent studies, a mixture of local domains with liquid-like weakly bonding and regions of solid-like strongly bonding exist in glassy alloys [3,4]. These imply that structural relaxation affects some local structure change and thermal stabilities of the bulk glassy alloys. Other approaches to improve materials features we suggest are electron and ion irradiation. We have been studying the radiation effects of electron and ion irradiation on the free volume and mechanical properties of ZrCuAl bulk glassy alloy [5,6,7]. In general, electron irradiation introduces vacancies and interstitials by local atomic displacement in crystalline metals. However, the radiation damage by energetic particles irradiation for the "bulk" glassy alloys has not been clarified yet. In this study, therefore, in order to study the influence of structural relaxation on radiation effect, we performed electron irradiation to as-quenched and structural relaxed $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys.

2. Experimental procedure

$Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloy was fabricated by the tilt casting method in an arc furnace and cut into the size of ϕ 6-8 mm × 0.5 mm disc [9]. Some of these quenched samples were annealed for 5 hours at 673 K, which is below glass transition temperature T_g [8]. All of these annealed and as-quenched samples were irradiated with 8 MeV electrons at room temperature by using an electron linear accelerator at the Research Reactor Institute, Kyoto University. The fluence of electron irradiation was from 2×10^{17} to 2×10^{18} e^-/cm^2. Positron annihilation lifetime and coincidence Doppler broadening (CDB) measurements were performed for these irradiated samples at room temperature. All the positron annihilation lifetime spectra were obtained by using a conventional fast-fast circuit with a time resolution of about 200 psec (FWHM) and analyzed by the POSITRONFIT program [10]. The positron annihilation spectra and CDB spectra consist of more than 10^6 and 10^8 counts, respectively. To confirm crystallinities of all samples due to irradiation, X-ray diffraction measurement was also performed using Rigaku Ultima IV.

3. Results and discussion

Figures 1 and 2 show X-ray diffraction spectra for as-quenched and structural relaxed $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys before and after electron irradiation. From these figures it can be seen for the range of electron irradiation fluences studied no crystalline peak were observed. The amorphous state is retained for both as-quenched and structural relaxed samples by electron irradiation.

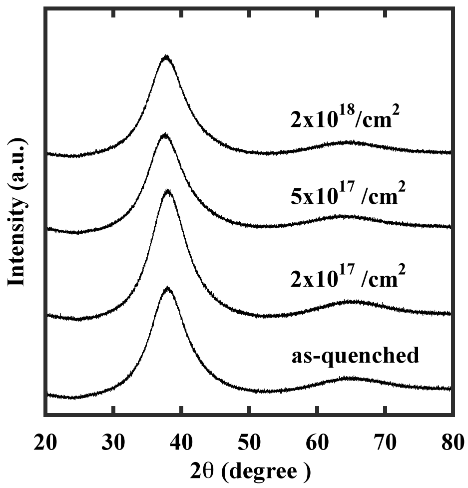

Figure 1. X-ray diffraction spectra for as-quenched $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys after electron irradiation.

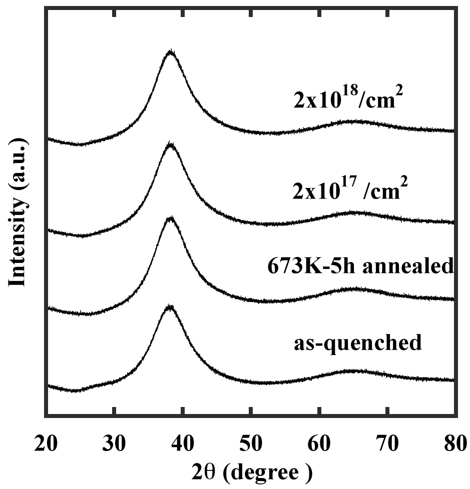

Figure 2. X-ray diffraction spectra for $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys with annealing followed by electron irradiation.

The mean positron lifetime value τ of as-quenched and structural relaxed samples are 166 and 157 psec, respectively. The positron lifetime decreases 9 psec by the annealing. This decreasing of positron lifetime reveals shrinkage of free volume by structural relaxation [8]. Figures 3 and 4 represent the change in positron lifetime τ by electron irradiation as a function of irradiation fluence for as-quenched and structural relaxed $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys. We fitted all the positron lifetime spectra with one, two, three components and the one component fits always had the lowest chi-squared. This indicates that the distribution of open volume size has single peak even though the samples are irradiated by electron. The positron lifetime increases with electron irradiation for both alloys. An increment of positron lifetime at maximum fluence of 2×10^{18} e^{-}/cm^{2} is about 10 psec for both cases. It can be estimated that electron irradiation introduces displacement defects for as-quenched and structural relaxed $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys. However, the increasing trend of positron lifetime with increase of irradiation fluence is clearly different between as-quenched and structural relaxed samples. In the case of as-quenched sample, the positron lifetime increases gradually at about 5×10^{17} e^{-}/cm^{2} irradiation as shown in Figure 3. On the other hand, in the case of structural relaxed one, the positron lifetime increases at low fluence of electron irradiation and its value is almost constant. From these results, following explanations can be given. In the case of as-quenched $Zr_{50}Cu_{40}Al_{10}$ alloys, the increasing in the size of free volume at low irradiation fluence is suppressed by formation of chemical short-range ordering (CSRO) through irradiation displacement at mainly liquid-like region in glassy alloy [3]. Actually, the formation of CSRO due to structural relaxation has been reported [11]. Above 1×10^{18} e^{-}/cm^{2} irradiation, no more CSRO formation takes place and it becomes vacancy type displacement damage that is retained. On the other hand, in the case of structural relaxed $Zr_{50}Cu_{40}Al_{10}$ alloys, after the initial increase further increases in the radiation fluence do not change the positron lifetime. This may suggest that no structural relaxation results from the irradiation because the liquid-like regions no longer exists due to annealing before irradiation.

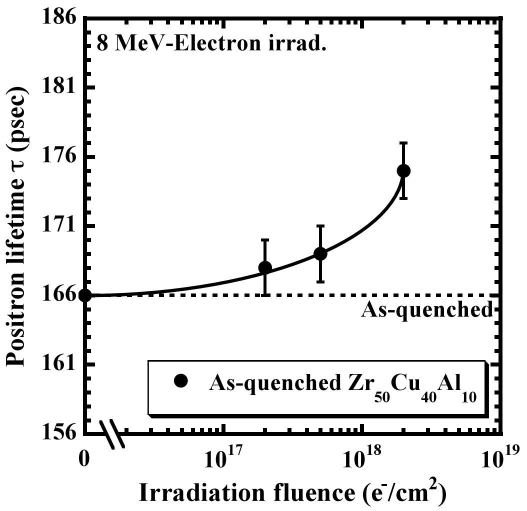

Figure 3. Change in positron lifetime τ by electron irradiation for as-quenched $Zr_{50}Cu_{40}Al_{10}$ as a function of irradiation fluence.

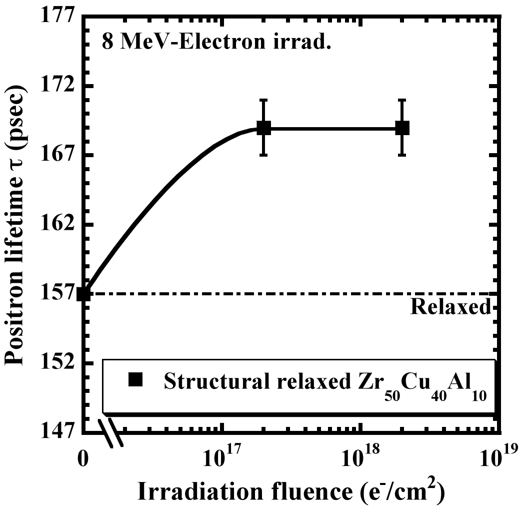

Figure 4. Change in positron lifetime τ by electron irradiation for structural relaxed $Zr_{50}Cu_{40}Al_{10}$ as a function of irradiation fluence.

Figures 5 and 6 show CDB profile before and after electron irradiation for as-quenched and structural relaxed $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys in the form of ratio of the CDB intensity to that for Al metal. CDB profile for ZrCuAl bulk glassy alloy does not change by structural relaxation [8], but it clearly changes by crystallization with long range atomic reordering [12]. No significant change in the CDB ratio profile with electron irradiation was observed for either type of sample. This suggests that long-range atomic reordering around free volume did not occur.

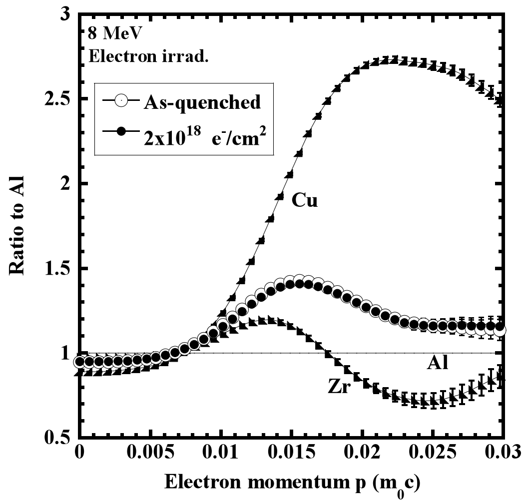

Figure 5. CDB ratio profile of as-quenched $Zr_{50}Cu_{40}Al_{10}$ with electron irradiation, expressed in the form of ratio to pure Al. CDB spectra of pure Zr and Cu are also plotted.

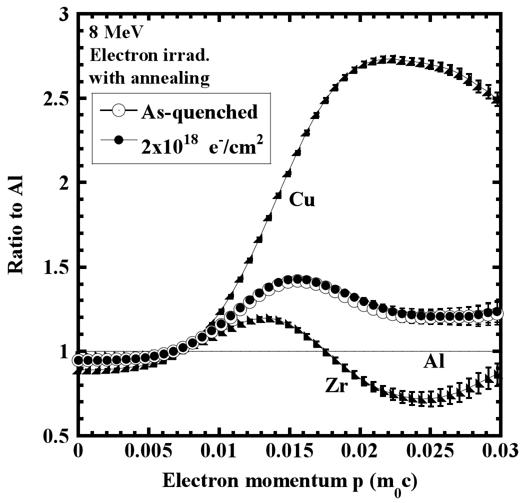

Figure 6. CDB ratio profile of structural relaxed $Zr_{50}Cu_{40}Al_{10}$ with electron irradiation, expressed in the form of ratio to pure Al. CDB spectra of pure Zr and Cu are also plotted.

4. Summary

The effect of structural relaxation on the radiation damage by electrons for $Zr_{50}Cu_{40}Al_{10}$ bulk glassy alloys was studied. We found that electron irradiation introduces the atomic displacements without crystallization. Moreover, we found that the structural relaxation by annealing before irradiation affects the radiation damage formation in this bulk glassy alloy by the electron irradiation especially at low fluence.

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