Electron irradiation damage and the recovery in a Zr-based bulk amorphous alloy Zr\textsubscript{55}Cu\textsubscript{30}Al\textsubscript{10}Ni\textsubscript{5}

K Sugita\textsuperscript{1}, M Matsumoto\textsuperscript{1}, M Mizuno\textsuperscript{1,2}, H Araki\textsuperscript{1,2}, Y Shirai\textsuperscript{1,2}

\textsuperscript{1}Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

\textsuperscript{2}Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

cuzuki.sugita@mat.eng.osaka-u.ac.jp

Abstract. Zr-based bulk amorphous alloys have been intensively studied because of their superiority in mechanical properties, corrosion resistance and micro-formability, and of great anticipation of their applications. The damage was introduced into a Zr-based bulk amorphous alloy Zr\textsubscript{55}Cu\textsubscript{30}Al\textsubscript{10}Ni\textsubscript{5} by electron irradiation below 20K. The thermal recovery process from the irradiation damage was studied by using positron lifetime spectroscopy which sensitively detect open volume defects. The introduced damage was completely recovered at the temperature lower than the glass transition temperature by 200K. On the other hand, the X-ray diffraction pattern shows no crystalline peaks even after the recovery of the irradiation damage. This result is considerably different from the previous reports studied in conventional amorphous alloys.

1. Introduction

Because Zr-based amorphous alloys have high glass forming abilities, the bulk amorphous materials can be formed. They show superior mechanical properties[1-5], corrosion resistance[1,6] and micro-formability[7], and have great anticipation of their applications[1]. So the origin of high glass forming abilities had been energetically studied both experimentally and theoretically. In this report the electron irradiation damage and its thermal recovery in a Zr-based bulk amorphous alloy Zr\textsubscript{55}Cu\textsubscript{30}Al\textsubscript{10}Ni\textsubscript{5} is studied by using positron lifetime spectroscopy. This method detects open volume defects sensitively and is used to investigate the mechanism of the defect relaxations and the short-range order atomic migration below the glass transition temperature.

2. Experimental

A 2.5mm thick plate of the amorphous alloy was fabricated by melting pure metals in an argon environment and then press-casting in a copper mold (Ishihara Corp., Nagano, Japan). The amorphous state of the as-cast alloy was confirmed by the X-ray diffraction (XRD). The samples were cut into 10\times10\times2.0 mm\textsuperscript{3} plates with a spark cutting-machining and subsequently polished with emery paper, then finally mirror-polished using a buff with 3\textmu m alumina slurry. To determine glass transition temperature and crystallization temperature of unirradiated sample, the differential thermal analysis (DTA) was performed in the temperature range of 300-950K with a heating rate of 0.667K/min using
Al₂O₃ as reference. The sample was irradiated below 20K with 990keV-electrons up to a total dose of 3.0×10¹⁸e-/cm².

Positron lifetime measurements for (1) irradiated and (2) unirradiated samples were carried out at room temperature during the isochronal annealing up to 853K. In case of the measurements for the irradiated sample, the positron source ²²NaCl (1 MBq) was sandwiched between as irradiated and as polished samples. The heat treatments were performed in a sealed silica tube. The positron lifetime spectrometer had a time resolution of 176ps (full width at half maximum) and each spectrum was accumulated to a total of 3×10⁶counts. The lifetime spectra were analyzed by using codes RESOLUTION [8] and POSITRONFIT EXTENDED [9,10]. XRD measurements were performed to identify the crystallization of the amorphous alloys with monochromatic CuKα radiation.

3. Results and discussion

3.1. Positron trapping in amorphous state

Positron lifetime for as polished sample was 169.7±0.2ps. This value is compared with our theoretical calculation; the value is longer than those expected for pure constituents of alloys, but shorter than those at metal vacancies. No lifetime component is found which is short enough to be attributed to non-trapped positrons. Additionally, the lifetime spectra from the sample are well fitted by only one exponential component. As discussed in Ref.11, these facts mean that practically all positrons are trapped and the corresponding lifetime value is characteristic of the trapping defects in the amorphous states.

3.2. Electron irradiation damage

Positron lifetime for as irradiated samples are listed in Table 1. As shown later by XRD profiles in Figure 5, the irradiated sample remains in an amorphous state. Then the increase in mean positron lifetime shows that some kinds of “defects” containing excess open volume are introduced in the bulk amorphous alloy by the electron irradiation. The multi-component analyses of positron lifetime spectra for as irradiated sample indicate the existence of longer lifetime component 189.4±5.0ps. But it does not exist for the unirradiated sample. This lifetime is longer than that of their constituent pure metals. The positron lifetime for randomly selected vacancies calculated by AT-SUP (atomic superposition) method [12] are shown in Figure 1. The details of the calculation method are given in our previous

|                  | τₚ (ps) | τ₀ (ps) | τ_d (ps) | I_d |
|------------------|--------|--------|----------|-----|
| (1) As polished  | 169.7  |        |          |     |
| (2) As irradiated| 177.7  | 117.8  | 189.4    | 0.81|

Table 1. Positron lifetime τₚ for (1) irradiated and (2) unirradiated samples. Longer positron lifetime component τ_d and its intensity I_d were fitted by two component analyses for the positron lifetime spectra of the irradiated sample.

Figure 1. Positron lifetime for zirconium-, aluminium-, copper- and nickel- sited vacancies in a Zr₅₅Cu₃₀Al₁₀Ni₅ amorphous alloy calculated by AT-SUP method. Five vacancy sites for each element were randomly selected for the calculation.
work [13]. The experimental value is approximately equal to those of copper- and nickel- sited vacancies in the amorphous alloy. These results suggest the defect production of relatively well-localized vacancy-like defects. In the primary stage single vacancy type defects are supposed to be created by electron irradiation at low temperature, then in the next defect relaxation process defects delocalize and be distributed among neighboring atoms. However, enough excess open volume remains even after the defect relaxation. Additionally, our brief estimation of the cross-sections predicts that copper- and nickel-sited vacancies can be predominantly created by 990keV electrons. The increase in the mean positron lifetime due to the electron irradiation is attributed to the positron trapping to the single vacancy type defect with excess open volume compared to the initial amorphous states. These results agree with previous study [11, 14-17].

The two component analyses mean that the smaller lifetime component is $117.8 \pm 6.0$ps, and this is much lower than that of unirradiated sample. If there is no detrapping from the pre-existing defects, the smaller lifetime component $\tau_0$ should stay constant 169.7ps. The experimental results signify that in the amorphous alloys positrons should detrapp from the state trapped in the pre-existing defects and annihilate in the vacancy-type defects introduced by the electron irradiation. It may sound to conflict with the discussion in chapter 3.1. It is explained as follows: in the unirradiated sample, positrons should be trapped in the pre-existing defect. However in the irradiated sample, positrons should detrapp from the pre-existing defects. These annihilation characteristics imply that positron trapping in the pre-existing defects is rather shallow and that the concentration of the defects is high enough to trap almost all positrons.

3.3. Thermal recovery from irradiation damage

Positron lifetime change during isochronal annealing is shown in figure 3. The thermal recovery stage of the introduced defects is clearly observed. This means that stability of the vacancy-like defects introduced by electron irradiation is not widely dispersed. This sudden decrease in the positron lifetime is definitely different from the contentious decrease in previous reports [11] on the conventional amorphous alloys studied by irradiations. The one reason for the dispersion of the thermal stability of the defects is that the vacancies sited only to particular elements are created by 990keV electrons. The lifetime spectra for the irradiated sample were analyzed in terms of two lifetime components $\tau_0, \tau_D$ with relative intensities $I_0, I_D$. The larger lifetime component corresponding to the positron annihilation in the defects $\tau_0$ was determined by as irradiated sample and was fixed to
The variation of parameters $\tau_0$, $\tau_D$, $I_0$ and $I_D$ with annealing temperature is shown in Figure 3. In order to investigate the recovery behavior of the defect, the trapping rate $\kappa = \nu C_D$, where $\nu$ is the specific trapping rate and $C_D$ is the defect concentration, is calculated by the following equation: $\kappa = I_d (1/\tau_0 - 1/\tau_d)$. The positron trapping rate $\kappa$ proportional to the defect concentration is shown in Figure 4. The sudden decrease in $I_D$ clearly represents that the defects introduced by electron irradiation anneal out below 473K, which is 200K lower than the glass transition temperature, 680K, determined by DTA. The thermal recovery from the irradiation damage below $T_g$ is also reported previously [11, 14,15].

XRD patterns for the irradiated sample during the isochronal annealing are shown in Figure 5. Even after the thermal recovery from the damage, the irradiated sample remains in an amorphous state. The thermal recovery from the irradiation damage below the glass transition temperature are also reported in some papers. However in cases reported previously [11], the thermal recovery from the damage is not complete.

**Figure 3.** Annealing temperature dependence of positron lifetime parameters $\tau_0$, $\tau_D$, $I_d$ during the thermal recovery process. The lifetime component $\tau_d$ for the defects was fixed to 189.4ps. Dashed line indicates the positron lifetime for the unirradiated sample.

**Figure 4.** Change of positron trapping rate $\kappa$, proportional to the defect concentration.

**Figure 5.** XRD patterns in each state.
associated with crystallization. The difference in the thermal recovery properties can be explained; Firstly, the irradiation damage of the sample in this report is relatively limited because vacancies sited only to particular elements can be created due to the low-energy electron irradiation. Secondly, our sample has much higher glass forming ability compared to conventional amorphous alloys reported previously. These results come to the following conclusion. In the Zr-based amorphous, copper- and nickel-sited vacancies created by electron irradiation anneal out due to the short-range migration of copper and nickel below the glass transition temperature. In the recovery temperature some elements, probably Al and Zr atoms, cannot migrate, then crystallizations cannot occur.

The crystallization temperature $T_X$ was increased by the electron irradiation in this work. As indicated in Figure 5, the irradiated sample remained in an amorphous state even after the annealing at 773K, which is higher than the crystallization temperature for the unirradiated sample. The increase in $T_X$ caused by the irradiation was also reported previously [16, 17]. These results imply that the creation and the subsequent annihilation of the relatively low-concentrated defects may improve the local structure of the amorphous alloys, i.e. the thermal properties such as crystallization temperature.

4. Conclusions
The thermal recovery from the electron irradiation damage in a Zr-based bulk amorphous alloy Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ was investigated by using positron lifetime spectroscopy. The results lead to the following conclusions.
1. Single vacancy type defects are created by 990keV electron irradiation below 20K.
2. The defects introduced by the electron irradiation anneal out below the glass transition temperature without crystallization.
3. Pre-existing defects in the amorphous alloy act behave shallow and concentrated positron trapping sites.

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