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Positron Lifetime Studies for Ce-based Bulk Metallic Glasses

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Positron lifetime and coincident Doppler broadening (CDB) spectroscopy were conducted for $Ce_{70}Al_{10}Cu_{20}$ bulk metallic glass (BMG) to study the local atomic structure. A single component positron lifetime of ~246 ps corresponding to annihilation in the free volume intrinsic to the local structure of BMG glassy matrix was obtained. CDB spectroscopy revealed that the free volume is dominantly surrounded by Ce atoms. Positron lifetime for $Ce_{70}Al_{10}Cu_{20}$ BMG is much longer than that of $Ce_{68}Al_{10}Cu_{20}Nb_2$ BMG, which is caused by the diffusion of Nb atoms into the vacancy-sized free volumes in the Ce-Al-Cu matrix. In addition, the positron lifetime for Ce-Al-Cu BMG is much different from those of Ce-Ga-Cu BMGs where two positron lifetime components $\tau_1 \sim 129$ ps and $\tau_2 \sim 261$ ps attributable to the densely-packed glassy state and free volume, respectively, are found. The present results imply that Ga plays an important role in triggering off the formation of the densely-packed glassy state.

1. Introduction

Metallic glasses are non-crystalline solids formed by continuous cooling from their melting liquids [1]. The free volumes introduced upon quenching are defined as open-volume defect-like regions in the glass matrix and regarded as playing an important role in their mechanical properties, thermodynamic features, atomic diffusivity, and atomic packing state [2–4]. The presence of free volume has been evidenced from the results of thermal relaxation [5], mass density [6], length change [7, 8], and direct probing with positrons [9]. Positron annihilation spectroscopy has been proven to be a powerful tool for investigations of open volume in metallic glasses [10–13], since positrons in condensed matter preferentially localize in regions of reduced atomic density and undergo annihilation with electrons. A single component positron lifetime of ~180 ps has been observed for Zr-based multicomponent metallic glasses, signifying the presence of vacancy-sized free volumes in the glass matrix [10–13]. Ce-based bulk metallic glasses (BMGs) have attracted considerable scientific and technological interests in the past decades due to their low glass transition temperature (T_g), excellent glass-forming ability, polyamorphism transition as well as heavy fermion behaviors [14–21]. In this work, positron lifetime spectroscopy was conducted for Ce-Al-Cu BMG and the result was compared with those of Ce-Al-Cu-Nb and Ce-Ga-Cu BMGs.

2. Experimental procedures

Master alloy ingots with nominal atomic percent composition of $Ce_{70}Al_{10}Cu_{20}$ were prepared by arc-melting mixtures of commercial-purity Ce (99.5 wt%), high-purity Cu (99.99 %), Al (99.99 %) metals in a purified argon atmosphere. The ingot was remelted more than four times and suction-cast into a Cu-mold to prepare a bulk glassy rod with a diameter of 2 mm. The amorphous state of the as-cast sample was confirmed by X-ray diffraction (XRD) using a D/MAX2500V diffractometer

Table I Positron lifetimes for $Ce_{70}Al_{10}Cu_{20}$, $Ce_{68}Al_{10}Cu_{20}Nb_2$ [23] and $Ce_{70}Ga_{10}Cu_{20}$ [23] BMGs. Positron lifetimes τ_1 and τ_2 are ascribed to annihilation in defect-free regions and vacancies, respectively, and I_1 and I_2 are their corresponding intensities. For comparison, positron lifetimes in defect-free regions ($\tau_{\text{Defect-free}}$) and monovacancies ($\tau_{\text{Monovacancy}}$) for several pure metals are also shown.

Samples	τ_1 [ps] (Defect free)	I_1 [%] (Defect free)	τ_2 [ps] (Vacancy)	I_2 [%] (Vacancy)
$Ce_{70}Al_{10}Cu_{20}$	—	—	245.7 ± 2	100 ± 1.5
$Ce_{68}Al_{10}Cu_{20}Nb_2$	—	—	213 ± 2	100 ± 1.5
$Ce_{70}Ga_{10}Cu_{20}$	129.1 ± 2	19.2 ± 1.5	261.0 ± 2	80.8 ± 1.5

Pure metals	$\tau_{\text{Defect-free}}$ (ps)	$\tau_{\text{Monovacancy}}$ (ps)
Ce [24]	197 ± 2	315 ± 2
Al [24]	165 ± 2	250 ± 2
Ga [24]	165 ± 2	238 ± 2
Cu [24]	105 ± 2	178 ± 2

with Cu K_α radiation at 40 kV. In contrast to the Ce-Ga-Cu BMG system [16], stable BMG was not available in a wide composition range for the Ce-Al-Cu system.

Positron lifetime and coincident Doppler broadening (CDB) spectroscopy experiments were performed at room temperature. The positron source (^{22}Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich for the measurements. Positron lifetime spectra ($\sim 1 \times 10^6$ coincidence counts) were recorded with digital oscilloscope-based system, in which a time resolution of 190 ps full-width at half-maximum (FWHM) was achieved. The positron lifetime spectra were numerically analyzed using the POSITRONFIT code [22]. The source component of ~10 % obtained from the result of RESOLUTIONFIT [21] analysis for well-annealed pure Al (purity 99.9999 wt%) was corrected along with background subtraction. For CDB spectroscopy, the energies of the two annihilation quanta E_1 and E_2 were measured with a collinear set-up of two high-purity Ge detectors. The spectra were obtained by cutting the E_1, E_2 spectra along the energy conservation line $E_1 + E_2 = (1022 \pm 1)$ keV, taking into account annihilation events within a strip of ±1.6 keV.

3. Results and discussion

Figure 1 shows the positron lifetime spectrum obtained for $Ce_{70}Al_{10}Cu_{20}$ BMG, which yields a single component positron lifetime. Table I lists the positron lifetimes of $Ce_{70}Al_{10}Cu_{20}$, $Ce_{68}Al_{10}Cu_{20}Nb_2$ [23] and $Ce_{70}Ga_{10}Cu_{20}$ [23] together with those at defect-free region and monovacancy of relevant pure metals [24]. The positron lifetimes for the defect-free region and monovacancy of face-centered cubic (f.c.c.) Ce, the main constituent of the present Ce-based BMGs, are 197 ps and 315 ps, respectively [24]. The positron lifetime $\tau_2 \sim 246$ ps observed for $Ce_{70}Al_{10}Cu_{20}$ BMG is longer than that of the defect-free matrix f.c.c. Ce and is shorter than that of monovacancy. It is thus expected that the vacancy-sized free volumes with a size slightly smaller than that of Ce monovacancy are present in $Ce_{70}Al_{10}Cu_{20}$ BMG. In the light of the fact that positron saturation trapping occurs, the concentration of vacancy-sized free volume could be higher than 10^{-4} in the atomic concentration. Vacancy-sized free volumes have been exclusively detected as a dominant atomic site in metallic glasses, such as Zr-based BMGs [10–13]. Such a local atomic structure could originate from the conventional random packing concept of amorphous alloys, being an intrinsic structural component of the glassy matrix in metallic glasses.

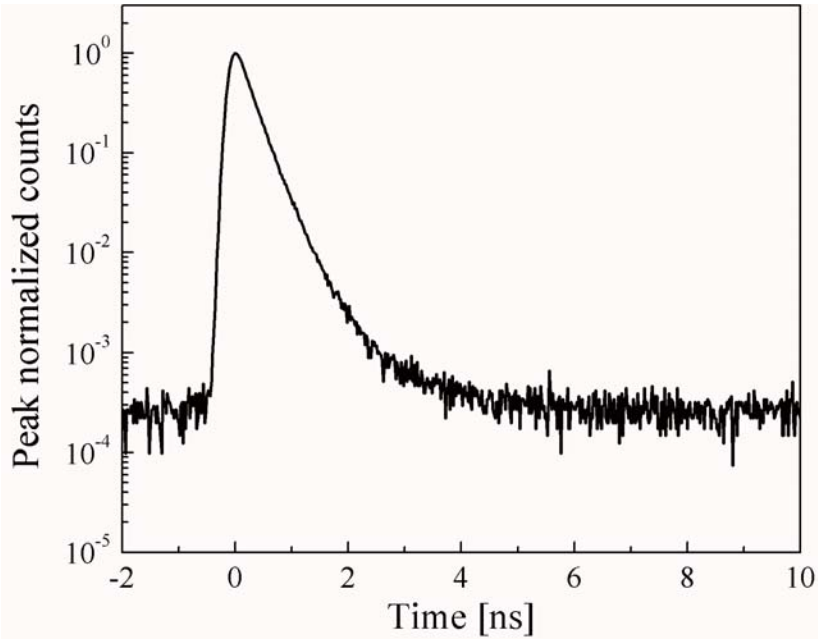

Fig. 1 Positron lifetime spectrum for $Ce_{70}Al_{10}Cu_{20}$ BMG.

Figure 2 shows the CDB spectra for $Ce_{70}Al_{10}Cu_{20}$ BMG together with those of pure Cu and Al metals. Here, the ratio spectra normalized to that of pure Ce are presented to highlight the difference of element-specific spectral shape in the higher-momentum core-electron region. The ratio spectrum for pure Ce thus corresponds to Y = 1. Spectrum of $Ce_{70}Al_{10}Cu_{20}$ BMG is essentially identical to that of pure Ce in the higher momentum region. This demonstrates that the elemental environment of the vacancy-sized free volumes revealed by positron lifetime spectroscopy is dominated by Ce atoms.

In our previous work on $Ce_{68}Al_{10}Cu_{20}Nb_2$ BMG, a single positron lifetime $\tau_2 \sim 213$ ps [23] much shorter than that of $Ce_{70}Al_{10}Cu_{20}$ was obtained. It is of interest that critical glassy rod diameter of $Ce_{70}Al_{10}Cu_{20}$ is drastically enhanced from 2 mm to 8 mm after Nb substitution for 2 at% Ce [14]. As revealed in the present work, the Ce-surrounding vacancy-sized free volumes in the amorphous matrix for Ce-Al-Cu BMG are slightly smaller than Ce monovacancy with the size of ~0.182 nm [25] in radius. Nb atoms with the size of ~0.146 nm [25] smaller than Ce atoms thus can diffuse into the vacancy-sized free volumes. Smaller open spaces after Nb substitution leads to shorter lifetime for $Ce_{68}Al_{10}Cu_{20}Nb_2$ BMG. When interstitial open spaces in the amorphous matrix are occupied by other atoms, the resistance of atomic diffusion increases and resultantly higher glass-forming ability (GFA) is obtained owing to high viscosity [5,26]. This could be the reason why GFA of $Ce_{70}Al_{10}Cu_{20}$ is drastically enhanced after addition of Nb.

As listed in Table I, positron lifetimes $\tau_1 \sim 130$ ps [23] shorter than that of the defect-free matrix of f.c.c. Ce were obtained for Ce-Ga-Cu BMGs in addition to the positron lifetimes τ_2 corresponding to annihilation in the free volumes. This is in sharp contrast with the result of positron lifetime spectroscopy obtained for $Ce_{70}Al_{10}Cu_{20}$ BMG (see above) and indicates the presence of atomically-concentrated site even more than that of f.c.c. Ce matrix. Our first-principles calculation predicted that the density of states of Ce-4f electron in Ce-Al-Cu BMG is more localized than that in Ce-Ga-Cu BMG [23]. This implies that the chemical pressure of Ga element partially induces delocalization transition from Ce-$4f^1$ to Ce-$4f^0$ state with the shortness of Ce-Ce distance. The present comparative studies of positron lifetimes between Ce-Al-Cu and Ce-Ga-Cu BMGs thus suggest that Ga plays an important role in triggering off the formation of the densely-packed glassy structure.

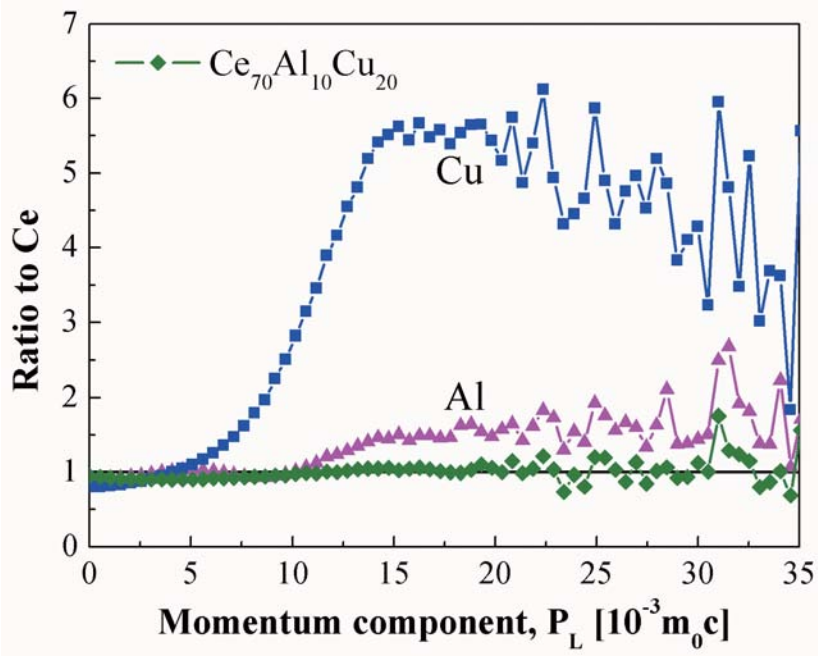

Fig. 2 CDB spectra of $Ce_{70}Al_{10}Cu_{20}$ BMG together with those of pure Cu and Al metals. Each spectrum is normalized to that of pure Ce (Y = 1).

4. Conclusion

$Ce_{70}Al_{10}Cu_{20}$ BMG was studied by positron lifetime spectroscopy and the result was compared with those of $Ce_{68}Al_{10}Cu_{20}Nb_2$ and $Ce_{70}Ga_{10}Cu_{20}$ BMGs. It was found the vacancy-sized free volumes in both $Ce_{70}Al_{10}Cu_{20}$, $Ce_{68}Al_{10}Cu_{20}Nb_2$ and $Ce_{70}Ga_{10}Cu_{20}$ BMGs, being an intrinsic structure of the glassy matrix in metallic glasses. Due to the diffusion of Nb atoms into the vacancy-sized free volumes, positron lifetime for $Ce_{68}Al_{10}Cu_{20}Nb_2$ is much shorter than that of $Ce_{70}Al_{10}Cu_{20}$. The Ce-concentrated glassy structures denser than that of f.c.c Ce were further observed in $Ce_{70}Ga_{10}Cu_{20}$ BMG. This anomalous packing state could arise from the shortness of Ce-Ce distance induced by the chemical pressure of Ga. The present results imply that Ga plays an important role in triggering off the formation of the densely-packed glassy structure.

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