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The role of open spaces to glass-forming ability in bulk metallic glasses

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ABSTRACT

Element-specific positron annihilation spectroscopy for Fe-B-Y-Nb bulk metallic glasses (BMGs) successfully sheds light on the role of interstitial open spaces in the amorphous matrix, as e.g., geometrically ideal open space, referred to as a Bernal hole, and large-scale nanovoids to glass-forming ability (GFA), yielding the following rules. Applying main constituent atoms in smaller sizes such as Fe, the Bernal holes get small without enhancing GFA since other elements cannot diffuse therein. On the contrary, main constituent atoms in larger sizes such as Ce form the large Bernal holes, which are feasible to accept other elements thus being responsible for GFA. The present findings is of pivotal importance in designing excellent BMGs with high GFA from the viewpoint of elemental combination of materials.

1. Introduction

Metallic glasses with an aperiodic amorphous structure, first discovered in 1960 [1], have stimulated great enthusiasm in their research due to their excellent magnetic properties, high corrosion resistance, and high mechanical properties [2–8]. However, the formation mechanism of bulk metallic glass (BMG) having higher glass-forming ability (GFA) has not been understood yet [9,10] for lack of local structural information inside the amorphous matrix, as e.g., interstitial open spaces. As a typical interstitial open space in the amorphous matrix of BMGs, one can easily speculate a Bernal hole considered in the dense random packing (DRP) model [11] that has been successfully applied to describe the prototype structures of metallic glasses [12–14]. By introducing the geometrically intrinsic Bernal holes, an ideal amorphous state with the maximum atomic density is available. Generally, such interstitial open spaces are the smallest open volume and slightly smaller than one-atom-missing open spaces such as monovacancy typically observed in the metals. Sietsma and Thijsse [15] have found that the intrinsic Bernal hole remained unchanged during annealing, but the larger holes were removed. Another open space is nanometer-sized quenched-in free volume, called as nanovoid, which is introduced upon rapid solidification [13] and sometimes by plastic deformation [16]. Such large-scale nanovoids in the amorphous matrix are generally in the thermally metastable state and could thus annihilate by long-term annealing.

Positron, antiparticle of electron, has proven to be a powerful tool for probing the above-mentioned open spaces [17–21]. A fraction of energetic positrons injected into the condensed matter preferentially localize in regions of reduced atomic density and undergo annihilation with electrons therein. Positron lifetime is very sensitive to the difference in electron density. In metallic elements, the positron lifetime increases in proportion with the size of vacancy when they are small as agglomeration of a few monovacancies, since the positron wave function can localize entirely in it. The reduced core electron density causes a deficit of annihilations with electrons having large momenta, which results in a narrowing of the electron-positron momentum density spectrum named as coincident Doppler broadening (CDB) spectroscopy. The measurements of positron lifetime by positron lifetime spectroscopy and momentum distribution of annihilation photons by CDB spectroscopy enable to obtain the information of the size of open spaces and their local chemical environment, respectively. In this work, an open space analysis utilizing positron lifetime and CDB spectroscopy was conducted for $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) BMGs, which are known to exhibit excellent GFA with strong Nb concentration dependence [22]. Based on the results of the present open space analysis and literature survey [13,18], the role of Bernal hole as well as large-scale nanovoid in the amorphous matrix to GFA is highlighted.

2. Experiments procedures

Master alloy ingots with nominal atomic percent compositions of $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) were prepared by arc-melting mixtures of high-purity Fe (99.99 wt.%), Y (99.9%), Nb (99.9%) and industrial Fe-B alloy (Fe ~ 78.61%; B ~ 20.32%) under the condition

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with a purified argon atmosphere. The ingots were remelted for more than four times and suction-cast into a Cu-mold to prepare bulk glassy rods with different diameters. The glassy nature of as-cast samples was confirmed by X-ray diffraction equipped with Cu $K\alpha$ as a radiation source at 40 kV. Diffraction scanning calorimetry (DSC) experiments were performed at a constant heating rate of 20 K/min. For estimating GFA, critical glass-forming diameters D_c were obtained as the maximum size in diameter when the fully glassy sample were prepared by copper-mold-casting technique. Furthermore the widths of supercooled liquid region ΔT_x ($= T_x - T_g$) were evaluated, since higher values of ΔT_x generally appears for the stabilized supercooled liquid region [23].

For positron lifetime and CDB measurements, the samples were cut into two identical disks with a thickness of 2 mm. The positron source (^{22}Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich. Positron lifetime spectra ($\sim 1 \times 10^6$ coincidence counts) were recorded with digital oscilloscope-based system, in which the time resolution of 190 ps full-width at half-maximum (FWHM) was achieved. The positron lifetime spectra were numerically analyzed using the POSITRONFIT code [24]. In 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 the annihilation events within a strip of $\pm$ 1.6 keV.

3. Results and discussion

Fig. 1 shows the DSC curves focusing on the glass transition and crystallization processes for $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) BMGs. All of the DSC traces exhibit broad endothermic peaks arising from glass transition, followed by exothermic reactions corresponding to the crystallization of the undercooled liquid. Onset temperatures of the glass transition (T_g) and the crystallization event (T_x) are displayed in Fig. 1 by arrows.

Positron lifetime spectroscopy yields a single component of positron lifetime τ_1 of ~176 ps for $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) BMGs, giving rise to positron saturation trapping. In Table 1, positron lifetimes for Fe-B-Y-Nb BMGs and a number of metallic glasses [13,18,25–28] previously reported are summarized together with those at defect-free region and monovacancy of pure Fe [29], Y [29] and Nb [29], and the values of D_c and ΔT_x [30,31]. The positron lifetime for the defect-free region of body-centered cubic (b.c.c.) Fe, the main constituent of the present BMGs, are 101 ps [29]. The positron lifetime $\tau_1 \sim 176$ ps observed for the Fe-B-Y-Nb BMGs is much longer than that of the defect-free matrix of b.c.c. Fe, but shorter than that of Fe monovacancy (~188 ps) [29]. It is thus expected that the presence of interstitial open spaces slightly smaller than that of Fe monovacancy for the Fe-B-Y-Nb BMGs. In light of the fact that positron saturation trapping occurs, highly concentrated interstitial open spaces with the atomic concentration of more than 10^{-4} are available in the amorphous matrix.

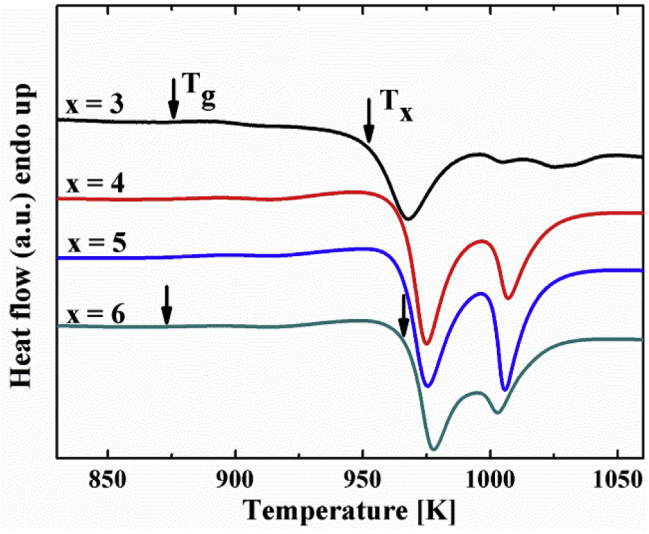

Fig. 1. DSC curves of $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) BMGs. Onset temperatures of the glass transition (T_g) and the crystallization event (T_x) are displayed by arrows.

Fig. 2 shows the results of CDB spectroscopy obtained for $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) BMGs together with those of pure Fe, B, Nb, and Y. Here, the ratio spectra normalized to that of pure Fe are presented to highlight the difference of element-specific spectral shape in the high-momentum core-electron region higher than 20×10^{-3} m_0c. The ratio spectrum for pure Fe thus corresponds to Y = 1. The spectral shapes of all the Fe-B-Y-Nb BMGs in the core electron region are similar to that of pure Fe (Y = 1) without any significant features arising from pure Nb, B, and Y (see solid lines). This demonstrates that the interstitial open spaces probed by positron lifetime spectroscopy is dominantly surrounded by Fe atoms.

As mentioned above, an ideal amorphous structure maximizing the local atomic density is obtained in the DRP model. The important structural feature of this model is the presence of interstitial open space region accompanied with Bernal holes that are necessary for the random packing of hard sphere in the amorphous matrix. In principle, such interstitial open spaces intrinsically available in the amorphous matrix are highly concentrated and slightly smaller than one-atom-missing open spaces such as monovacancy typically observed in the metals [28]. It is noted that the Fe-rich interstitial open spaces identified here are slightly smaller than Fe monovacancy with the high atomic concentration of more than 10^{-4}. They could be the geometrically ideal open spaces in the amorphous matrix with maximum atomic density, being the most probable candidate for the Bernal holes that have been long discussed within a framework of DRP model.

Fig. 3 shows Nb-concentration dependence of (a) positron lifetime τ_1, (b) width of supercooled liquid region ΔT_x, and (c) critical glass-forming diameter D_c for $(Fe_{71.2}B_{24}Y_{4.8})_{100-x}Nb_x$ (x = 3, 4, 5, 6) BMGs. No significant variations with Nb concentration is seen for positron lifetimes, which are consistent with the results of CDB spectroscopy (see Fig. 2). This implies that the local atomic and electronic structures of Bernal holes are not significantly influenced by Nb concentration. On the other hand, both ΔT_x and D_c exhibit the highest values at the Nb concentration of 4% achieving the highest GFA. The above comparative results capture the picture that the Bernal holes in the amorphous matrix do not contribute to GFA for the Fe-B-Y-Nb BMGs.

When interstitial open spaces in the amorphous matrix are occupied by other atoms, the resistance of atomic diffusion increases and resultantly higher GFA is obtained owing to high viscosity [32]. As revealed in the present work, the Fe-surrounding Bernal holes in the amorphous matrix for the Fe-B-Y-Nb BMGs are slightly smaller than Fe monovacancy with the size of ~128 p.m. [33] in radius. Nb atoms with the size of ~146 p.m. [33] larger than Fe atoms thus cannot diffuse into the Bernal holes, by which the variation of positron lifetime as well as the momentum distribution of annihilation photons are less effective to Nb concentration (see Figs. 2 and 3 (a)). This could be the reason why the geometrically ideal Bernal holes in the amorphous matrix do not contribute to GFA for the Fe-B-Y-Nb BMGs.

As for the enhancement of GFA observed in the data of thermal analysis in addition to critical glass-forming diameter (see Fig. 3 (b) and (c), and Table 1), we expect that interstitial open spaces larger than the Bernal holes, as e.g., nanovoid, are of significance. It is naturally presumed that Nb atoms easily diffuse into the large-scale nanovoids enhancing GFA. Here, there may arise the question why the large nanovoid cannot be obtained by positron lifetime spectroscopy. As demonstrated in this work, the present BMG system contains high concentration of open spaces with the atomic concentration of more than 10^{-4}. Under the condition of positron saturation trapping, an