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Effect of Al on the local structure and stability of Zr-based metallic glasses

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Abstract

The effect of Al addition on the local structure and the thermal stability in the Zr–Ni-based metallic glass is investigated. It is well known that Al is a very effective element on the enhancement of glass-forming ability (GFA), i.e., stability of supercooled liquid state in the alloy system. We have found that the dominant local structure is icosahedral-like in the $Zr_{70}Al_{10}Ni_{20}$ metallic glass and the tetragonal Zr_2Ni-like local in the $Zr_{70}Ni_{30}$ amorphous alloy. It is concluded that the change in the dominant local structure contributes to the enhancement of the stability of supercooled liquid state in the alloy.

Keywords: Metallic glasses; EXAFS; Atomic scale structure; X-ray diffraction; Quasicrystal

1. Introduction

Recent studies on the icosahedral quasicrystalline phase (I-phase) formation in several Zr-based metallic glasses with high GFA lead to the suggestion of the icosahedral local structure in the glassy state [1–4]. Very recently, we have reported the existence of icosahedral local structure in the Zr–Cu binary metallic glass as well as Zr-based multicomponent metallic glasses by structural analysis using X-ray diffraction XRD, transmission electron microscopy TEM and so on [5,6]. Moreover, it is suggested a strong correlation between the stability of supercooled liquid state and the icosahedral local structure in the glassy state [7]. It is well known that Al is very effective on the stability of supercooled liquid state in the Zr–Al–Ni metallic glasses [8]. In this study, the local structure of the $Zr_{70}Al_{10}Ni_{20}$ metallic glass is examined using detailed XRD and extended X-ray absorption fine structure (EXAFS) measurements. We intend to investigate the mechanism of the enhancement of the stability of supercooled liquid state and comparing to that in the $Zr_{70}Ni_{30}$ amorphous alloy.

2. Experimental procedures

Ribbon samples with a cross-section of 0.03 mm × 1 mm were produced by melt spinning of arc-melted $Zr_{70}Ni_{30}$ and $Zr_{70}Al_{10}Ni_{20}$ alloy ingots in an argon atmosphere. Thermal properties were measured with a differential scanning calorimeter (DSC) at a heating rate of 0.67 K s^{-1}. The local atomic structure was studied by X-ray diffraction measurements with Ag Kα radiation (50 kV to 30 mA) and a flat graphite counter monochromator. The observed diffraction profiles were corrected by the Krog–Moe–Norman method to obtain an interference function. The ordinary radial distribution function (RDF) was led by Fourier transformation of the interference function. EXAFS measurements for the analysis of the local environments around Zr and Ni atoms were performed on beam line BL-12C at the Photon Factory of the Institute of Materials Structure Science, High-Energy Accelerator Research Organization (KEK), Tsukuba, Japan. All the measurements were done in transmission geometry at room temperature. Measured spectra were analyzed using the program REX 2000 (Rigaku Corp.).

3. Results and discussion

Only the single exothermic peak with the onset temperature, T_x of 652 K is observed in the DSC curve of the $Zr_{70}Ni_{30}$ amorphous alloy. In contrast, significant glass transition (T_g = 636 K) and wide supercooled liquid region of approximately 66 K prior to the single crystallization peak (T_x = 702 K) are exhibited in the $Zr_{70}Al_{10}Ni_{20}$ metallic glass. These results indicate that the stability of supercooled liquid state is enhanced by the Al addition. The authors have previously pointed out the possibility

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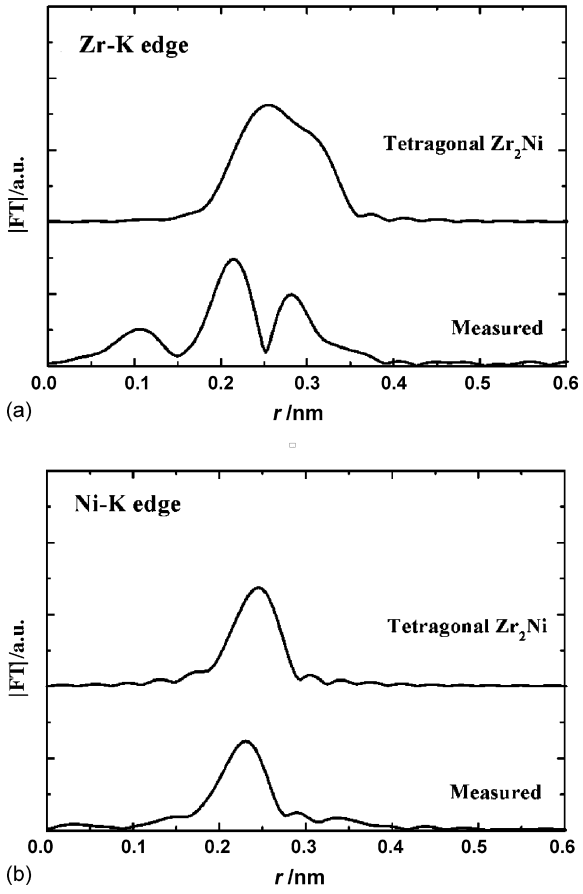

Fig. 1. Fourier transforms of the EXAFS results of the Zr K-edge (a) and Ni K-edge (b) in the $Zr_{70}Ni_{30}$ amorphous alloy.

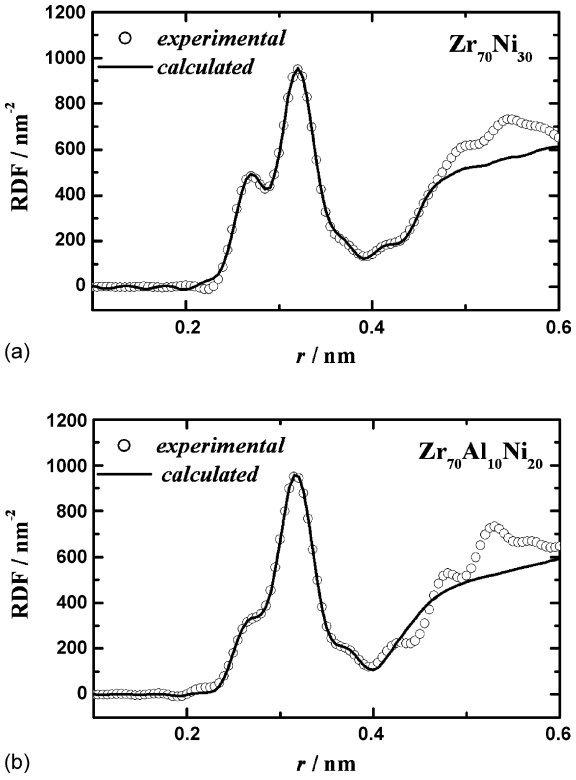

Fig. 2. Radial distribution functions (RDFs) of the $Zr_{70}Ni_{30}$ amorphous alloy (a) and $Zr_{70}Al_{10}Ni_{20}$ metallic glass (b).

of existence of tetragonal Zr_2Ni-like local environment in the $Zr_{70}Ni_{30}$ amorphous alloy in the radial distribution function (RDF) analysis [9], however, the details are not clear. In order to analyze the local environment around each of atom species, EXAFS measurements were performed. Fig. 1 shows the Fourier transformation curves of the experimental results of EXAFS measurements of the Zr K-edge (a) and Ni K-edge (b) in the $Zr_{70}Ni_{30}$ amorphous alloy. The calculated results of the tetragonal Zr_2Ni structure, which is the structure of the precipitated phase of the alloy, are also denoted for comparison. While the morphology of the curve of Zr K-edge in (a) is significantly different from that in the Zr_2Ni structure, both curves resemble each other in the Ni K-edge in (b), indicating that the Zr_2Ni-like local structure is formed around Ni atom in the $Zr_{70}Ni_{30}$ amorphous alloy.

The effect of Al on the local structure is investigated using RDF analysis and EXAFS measurements. Fig. 2 shows RDFs of the $Zr_{70}Ni_{30}$ amorphous alloy (a) and $Zr_{70}Al_{10}Ni_{20}$ metallic glass (b). By addition of Al, it is observed that the intensity of the first peak ($r \sim 0.26$ nm) decreases drastically. The first peak corresponds to the Zr–Ni pair, of which distance is smaller than that calculated from their atomic radii. Therefore we suggest the existence of strong local ordering of the tetragonal Zr_2Ni-like structure. Since the intensity of the first peak decreases significantly in the $Zr_{70}Al_{10}Ni_{20}$ metallic glass, it is recognized that the Zr_2Ni-like local structure is changed considerably by Al atoms addition. In fact, the coordination numbers of Zr–Zr and Zr–Ni are calculated to be 9.4 and 2.6 in the $Zr_{70}Ni_{30}$ amorphous alloy and 9.5 and 1.3 in the $Zr_{70}Al_{10}Ni_{20}$ metallic glass, respectively. It is noted that the decrease in the coordination number of Zr–Ni pair is more than the decrease in the Ni content by Al addition. We can conclude that the Al plays an important role for the decomposition of the Zr_2Ni-like local structure and the formation of novel local structure. Considering the primary I-phase formation by addition of a very small amount (~1 at.%) of noble metal such as Pd in the $Zr_{70}Al_{10}Ni_{20}$ metallic glass [10], we can also investigate the icosahedral-like local structure in the alloy. In order to examine the local structural similarity, we performed EXAFS measurements for the $Zr_{70}Al_{10}Ni_{20}$ and $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glasses. The Fourier transforms of EXAFS results of the as-quenched $Zr_{70}Al_{10}Ni_{20}$ and $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glasses and the quasicrystal (QC)-formed $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glass annealed for 900 s at 670 K are shown in Fig. 3. For the Zr K-edge (a), no significant differences are observed between the $Zr_{70}Al_{10}Ni_{20}$ and $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glasses in the as-quenched state. However, the peak intensities of the first and second shells for the annealed state of the $Zr_{70}Al_9Ni_{20}Pd_1$ sample is reversed compared to that in the as-quenched state. Here, the second shell consists of pairs of Zr–Zr (major) and Zr–Al (minor), considering their distances and coordination numbers. The increase in the peak intensity of the second shell is attributed to the slight rearrangement of Zr around Zr atoms. In the Fourier transformations of the Ni K-edge data (b), no obvious shift is exhibited

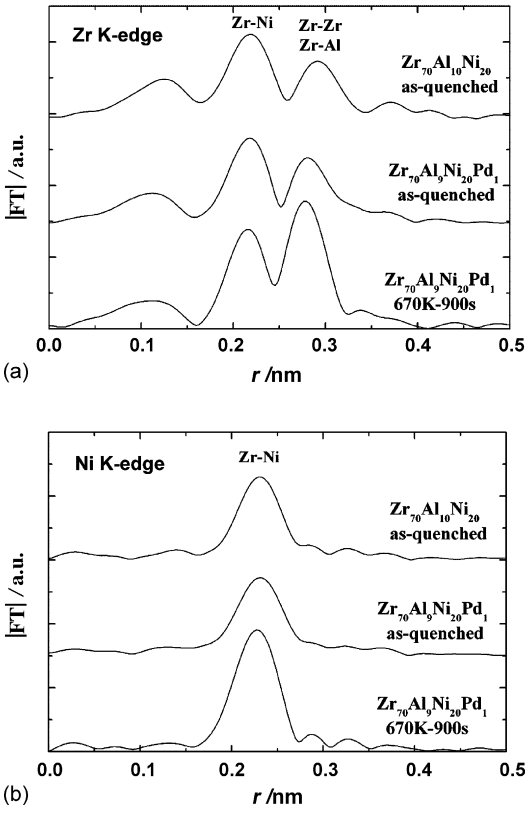

Fig. 3. Fourier transforms of EXAFS results of the as-quenched $Zr_{70}Al_{10}Ni_{20}$ and $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glasses and the QC-formed $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glass annealed for 900 s at 670 K.

by the main peak for the as-quenched states of the $Zr_{70}Al_{10}Ni_{20}$ and $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glasses. For the annealed sample, the profile becomes sharper, which can be attributed to ordering occurring in the first coordination shell. However, the shape of profile for the annealed sample is quite similar to that of the as-quenched one. Therefore, we conclude that the change in local environment around Ni atom is small following quasicrystallization in the annealed state as well as on Pd addition in the as-quenched glassy state. It is also concluded that the local environment in the glassy state does not change by the addition of 1 at.% Pd to $Zr_{70}Al_{10}Ni_{20}$ metallic glass, even though the propensity to form quasicrystals is significantly enhanced. It is proposed that a common local structure exists between the $Zr_{70}Al_{10}Ni_{20}$ metallic glass and the I-phase. Considering the corresponding atomic configurations, we suggest that icosahedral order is the common local structure.

4. Conclusions

We investigated the effect of Al on the local structure in the $Zr_{70}Al_{10}Ni_{20}$ metallic glass with a stable supercooled liquid state. We have found that the dominant local structure in the alloy is different from the tetragonal Zr_2Ni-like local structure in the $Zr_{70}Ni_{30}$ amorphous alloy. Considering the local structure of $Zr_{70}Al_{10}Ni_{20}$ metallic glass and the QC-forming $Zr_{70}Al_9Ni_{20}Pd_1$ metallic glass, it is found that the dominant local environment remains unchanged by the addition of Pd in the as-quenched state and also by QC-formation on annealing, which indicates that quasicrystallization proceeds without any significant rearrangement of the constituent elements. A common icosahedral local structure is proposed. Therefore, we suggest a correlation between the stability of the supercooled liquid state and the icosahedral local structure in alloys containing elements such as Zr, Al and Ni, which have strong chemical affinities for each other.

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