Comparative Study on Glassy Phase Stabilities of Zr–Co–Al and Zr–Ni–Al Metallic Glasses

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The phase stabilities of Zr–Co–Al and Zr–Ni–Al metallic glasses have been investigated by the thermal analysis and compared with each other. It is found that the largest $\Delta T_x$, $T_g/T_l$ and $y$ parameters of the former are larger than those of the latter, indicating that the former have higher glassy phase stability than the latter. It is also found that the optimum compositions of the former are Zr-poorer and Al-richer than those of the latter and that their transition metal compositions are almost the same. Since Co and Ni have almost the same atomic radius and mixing enthalpy against Zr which are factors correlated with the glassy phase stability, this composition difference may be attributable to another factor, i.e. their difference of the electronic contribution due to the different electronic structure around the Fermi level.

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1. Introduction

Many researchers have investigated the glassy phase stability of metallic glasses. There are several kinds of parameters which are concerned with the phase stability of the metallic glasses. The most well-known one is the supercooling liquid region: $\Delta T_x$ which is equal to the difference between the glass transition temperature: $T_g$ and the crystallization temperature: $T_x$, i.e. $\Delta T_x = T_x - T_g$. Most of the papers reported so far on the phase stability of the metallic glasses showed the composition dependence of this parameter. For example, Inoue et al. reported the composition dependence (mapping) of the $\Delta T_x$ of the ternary Zr–Ni–Al metallic glasses.¹) Another important and well-known parameter is the ratio between the glass transition temperature and liquidus temperature: $T_l$ / $T_x$, i.e. $T_g/T_l$. Recent papers on the phase stability of the metallic glasses also reported on the composition dependence of this parameter as well as $\Delta T_x$. For example, Yokoyama et al. reported the composition dependence (mapping) of these parameters of the Zr–Cu–Al ternary metallic glasses.²) There is also another important parameter: $y$ which is recently proposed by Lu and Liu.³) This is defined by the equation of $T_l/(T_g + T_l)$. This is also an important parameter concerned with the glassy phase stability and is discussed in the recent papers.

In this manuscript the glassy phase stability of the Zr–Co–Al and Zr–Ni–Al ternary metallic glasses are investigated because the Zr–LTM–Al (LTM: late 3d transition metal) ternary metallic glasses are important mother alloys to develop new Zr-based multicomponent ones. Here, Co and Ni are neighbouring elements in the periodic table. Besides, they have the same atomic radius (0.125 nm) and also almost the same mixing enthalpy against Zr, which is main component, Co: $-41$ kJ/atom, Ni: $-49$ kJ/atom. Here, the atomic radius and the mixing enthalpy are important factors to dominate the glassy phase stability of the metallic glass. In this study, the composition dependences of the three parameters mentioned above are clarified for the Zr–Co–Al and Zr–Ni–Al ternary metallic glasses. The three parameters of these ternary alloy systems are compared to one another. Besides, the results in each ternary alloy system are compared to each other and discussed from the viewpoint of their electronic structure.

2. Experimental Procedure

Alloy ingots were prepared in the arc-melting furnace in a purified argon atmosphere. Metallic glasses were prepared by the conventional single-roll spinning method in a purified argon atmosphere. The as-prepared ribbons were of about 1 mm in width and 20 µm in thickness. Glassy phase was identified by the X-ray diffraction method using a monochromatized Cu-Kα radiation. Thermal stability was investigated by the differential scanning calorimetry (DSC) in a flow of purified argon atmosphere. The heating rate during the DSC measurement was about 0.67 K/s. The liquidus temperature was determined by the differential thermal analysis (DTA) in a flow of purified argon atmosphere. The cooling rate during the DTA measurement was about 0.083 K/s.

3. Results and Discussion

Figure 1 shows one of the typical X-ray diffraction patterns of the as-spun ribbons. This pattern shows a single halo pattern, indicating a single glassy phase. Figure 2 shows one of the typical DSC curves of the prepared metallic glasses. There is an endothermic phenomenon below the clear exothermic first peak. These correspond to the glass transition and the crystallization, respectively, of which temperatures are indicated by $T_g$ and $T_x$ in the figure. Figure 3 shows one of the typical DTA curves of the prepared metallic glasses. There are three exothermic peaks and the highest peak temperature corresponds to the liquidus temperature indicating by $T_l$ in the figure. The three important parameters concerned with the glassy phase
stability, $\Delta T_x$, $T_g/T_1$, $\gamma = T_g/(T_g + T_1)$, can be estimated by these results.

Figure 4 shows the composition dependence of the three parameters for the Zr–Co–Al metallic glasses. The surrounding relevant compounds are also marked in the figures. The largest $\Delta T_x$, 81 K, is obtained at the composition of Zr$_{55}$Co$_{25}$Al$_{20}$. The $\Delta T_x$ decreases gradually along the tie-lines from this composition to Zr$_2$Co and ZrCo compound compositions. On the other hand, it is found that it decreases rapidly along the tie-lines to Zr$_6$CoAl$_2$ and ZrCoAl compound compositions. The largest $T_g/T_1$ is 0.640 and obtained at the composition of Zr$_{50}$Co$_{25}$Al$_{25}$. Compared to the largest $\Delta T_x$ composition, this is slightly Zr-poor and Al-rich but just near the composition. The $T_g/T_1$ decreases in the same way as the composition dependence of the $\Delta T_x$. The largest $\gamma$ is 0.420 and obtained at the composition of Zr$_{55}$Co$_{25}$Al$_{30}$. This is the same composition at which the largest $\Delta T_x$ is also obtained. The $\gamma$ parameter also decreases in the same way as the composition dependences of the former two parameters. These results indicate that the largest parameter composition and qualitative composition dependence of the parameter of the Zr–Co–Al metallic glasses hardly depend on the parameter. Therefore, it can be concluded that the metallic glasses around the Zr$_{55}$Co$_{25}$Al$_{20}$ and Zr$_{50}$Co$_{25}$Al$_{25}$ compositions have the highest glassy phase stability in the Zr–Co–Al alloy system.

Figure 5 shows the composition dependence of the three parameters for the Zr–Ni–Al metallic glasses. The surrounding relevant compounds are also marked in the figures. The largest $\Delta T_x$, 69 K, is obtained at the composition of Zr$_{65}$Ni$_{20}$Al$_{15}$. The $\Delta T_x$ decreases gradually along the tie-lines from this composition to Zr$_5$Ni and Zr$_5$Ni$_3$Al compound compositions. On the other hand, it is found that it decreases rapidly along the tie-lines to Zr$_6$NiAl$_2$ and ZrNiAl compound compositions. The largest $T_g/T_1$ is 0.603 and obtained at the composition of Zr$_{60}$Ni$_{25}$Al$_{15}$. Compared to the largest $\Delta T_x$ composition, this is slightly Zr-poor and Ni-rich but just near the composition. The $T_g/T_1$ decreases in the same way as the composition dependence of the $\Delta T_x$. The largest $\gamma$ is 0.412 and obtained at the composition of Zr$_{60}$Ni$_{25}$Al$_{15}$. This is the same composition at which the largest $\Delta T_x$ is also obtained. The $\gamma$ parameter also decreases in the same way as the composition dependences of the former two parameters. These results indicate that the largest parameter composition and qualitative composition dependence of the parameter of the Zr–Ni–Al metallic glasses hardly depend on the parameter as well. The Zr–Co–Al alloy system. Therefore, it can be concluded that the metallic glasses around the Zr$_{60}$Ni$_{25}$Al$_{15}$ and Zr$_{65}$Ni$_{20}$Al$_{15}$ compositions have the highest glassy phase stability in the Zr–Ni–Al alloy system.

Although the largest value of three parameters is obtained at almost the same composition, their composition distribution depends slightly on the parameter. This is attributable to the following characteristics of the definition of each parameter. The first parameter $\Delta T_x = T_x - T_g$ means the
crystallization tendency upon heating a glass. That is, a large \( \Delta T_x \) indicates a high resistance to the nucleation and growth of crystallizing phases. On the other hand, the second parameter, so-called reduced glass transition temperature; \( T_g/T_l \) indicates a small temperature region between \( T_g \) and \( T_l \) upon decreasing a liquid. Therefore, the \( T_g/T_l \) parameter means the solid amorphization tendency of the liquid. The third one, \( \gamma \) is defined as \( \gamma = (T_g/T_x + T_l)/T_x \).

Fig. 4 The composition dependence of the three parameters concerned with the glassy phase stability for the Zr–Co–Al metallic glasses. The surrounding relevant compounds are also marked in the figures. Black solid marks mean the sample compositions in this study. (a) \( \Delta T_x \), (b) \( T_g/T_l \), (c) \( \gamma \)
They argued that $\gamma$ is a parameter proposed from the perspectives of both crystallization and amorphization because two factors, $T_g/T_x$ and $T_l/T_x$, in this parameter are related with the crystallization and amorphization, respectively. Therefore, they concluded that $\gamma$ was the best parameter to estimates the glass forming
ability. Since three parameters have these perspective characteristics different from one another, the composition distribution of the parameters depends on them.

It is noteworthy to compare the results between the Zr–Co–Al and Zr–Ni–Al metallic glasses because Co and Ni are neighboring elements in the periodic table and have the same atomic radius and almost the same mixing enthalpy against Zr, which is main component of the alloys, as mentioned in the introduction. At first, the largest three parameters concerned with the glassy phase stability, which are summarized in Table 1, are discussed. It is found that all of the largest parameters of the Zr–Co–Al metallic glasses are larger than those of the Zr–Ni–Al ones. This means that the former have higher glassy phase stability than the latter. The next notable point is the optimum composition (Table 1) at which the largest parameters are obtained. It is found that the optimum composition of the Zr–Co–Al metallic glasses is Zr-poorer and Al-richer than that of the Zr–Ni–Al ones and that their transition metal compositions are almost the same. Accordingly, the contour position of the three parameters of the former in Fig. 4 shifts to the Zr-poorer and Al-richer composition region compared to that of the latter in Fig. 5 although the contour appearance is similar between both metallic glasses. Here, it should be noted insistently that two important factors concerned with the glassy phase stability: the atomic size of Co and Ni and their mixing enthalpy against Zr, are almost the same as each other. Therefore, the difference of the phase stability between the Zr–Co–Al and Zr–Ni–Al metallic glasses mentioned above indicates that there is another important factor leading to the difference. The most possible another factor for the phase stability is the contribution of the electronic system, such as the Hume–Rothery-type stabilization in which the e/a value is an important parameter. Therefore, it is interesting to estimate the e/a value of the optimum composition of both alloy systems. The e/a values of the averaged optimum compositions: Zr$_{53.3}$Co$_{25}$Al$_{20}$ and Zr$_{61.7}$Ni$_{23}$Al$_{15}$ are 1.4505 and 1.3405, respectively. Here, the values of 1.5, 0, 0 and 3 are assigned to the electron number of Zr, Co, Ni and Al, respectively. Since these values are clearly different from each other, the simple Hume–Rothery scheme on the basis of the rigid band model cannot be applied to explain this optimum composition difference although Co and Ni are neighbours in the periodic table. This strongly suggests that the electronic structure around the Fermi level of the Zr–Co–Al and Zr–Ni–Al metallic glasses are clearly different from each other.

The electronic structure of Zr–Co and Zr–Ni metallic glasses were already reported experimentally by Oelhafen et al. They reported the varying d-band splitting in the electronic structure of the Zr-LTM binary metallic glasses. They have clarified that the Zr-4d band is located at almost the same energy level as the Fermi level. They have also clarified that the Co-3d band is located at about 1.4 eV higher binding energy to the Fermi level. On the other hand, it has been reported that the Ni-3d band is located at about 2.0 eV higher binding energy to the Fermi level. This relative binding energy situation of the Zr-4d, Co-3d and Ni-3d bands result in the almost single d-band for the density of states of the Zr–Co metallic glasses and the split d-band for that of the Zr–Ni ones. Sada et al. recently reported valence-band photoelectron spectra of Zr$_{53}$Cu$_{30}$Ni$_{15}$ quaternary bulk metallic glass. They have clarified that the Ni 3d and Cu 3d states are located at the binding energy of about 2.0 eV and about 3.7 eV, respectively. These are almost the same binding energy as the Ni 3d state (≈2.0 eV) and Cu 3d one (≈3.5 eV) of the binary Zr–Ni and Zr–Cu metallic glasses reported by Oelhafen et al. These results suggest that the Co 3d and Ni 3d states of the ternary Zr–Co–Al and Zr–Ni–Al metallic glasses are located at almost the same binding energy of those of the binary Zr–Co and Zr–Ni ones, i.e. almost single d-band for the Zr–Co–Al metallic glasses and the split d-band for that of the Zr–Ni–Al ones as well as the binary Zr–Co and Zr–Ni ones. Accordingly, this difference may be the reason for the different optimum electron number, i.e., e/a value, and subsequently the different optimum alloy composition for the glassy phase stability between the Zr–Co–Al and Zr–Ni–Al metallic glasses.

### 4. Conclusion

The phase stabilities of the Zr–Co–Al and Zr–Ni–Al metallic glasses have been investigated by the thermal analysis. The largest $\Delta T_g$, $T_g/T_i$ and $\gamma$ of the Zr–Co–Al metallic glasses are 81 K, 0.640 and 0.420, respectively. They are obtained at the composition of Zr$_{53}$Co$_{25}$Al$_{20}$, Zr$_{50}$Co$_{25}$Al$_{15}$ and Zr$_{55}$Co$_{25}$Al$_{15}$, respectively. Therefore, the metallic glasses around the Zr$_{53}$Co$_{25}$Al$_{20}$ and Zr$_{50}$Co$_{25}$Al$_{15}$ compositions have the highest glassy phase stability in the Zr–Co–Al alloy system. The largest $\Delta T_g$, $T_g/T_i$ and $\gamma$ of the Zr–Ni–Al metallic glasses are 69 K, 0.603 and 0.412, respectively. They are obtained at the composition of Zr$_{60}$Ni$_{25}$Al$_{15}$, Zr$_{65}$Ni$_{25}$Al$_{15}$ and Zr$_{65}$Ni$_{20}$Al$_{15}$, respectively. Therefore, the metallic glasses around the Zr$_{60}$Ni$_{25}$Al$_{15}$ and Zr$_{65}$Ni$_{20}$Al$_{15}$ compositions have the highest glassy phase stability in the Zr–Ni–Al alloy system. It is found that all of the largest parameters of the Zr–Co–Al metallic glasses are larger than those of the Zr–Ni–Al ones. This means that the former have higher glassy phase stability than the latter. It is found that the optimum composition of the Zr–Co–Al...
metallic glasses is Zr-poorer and Al-richer than that of the Zr–Ni–Al ones and that their transition metal compositions are almost the same. Accordingly, the contour position of the three parameters of the former shifts to the Zr-poorer and Al-richer composition region compared to that of the latter although the contour appearance is similar between both metallic glasses. Since Co and Ni have almost the same atomic radius and mixing enthalpy against Zr which are factors correlated with the glassy phase stability. This difference may be attributable to the difference of the electronic contribution to the glassy phase stability because of the different electronic structure around the Fermi level between the Zr–Co–Al and Zr–Ni–Al metallic glasses.

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REFERENCES