Formation, Thermal Stability and Mechanical Properties in Zr–Al–Co Bulk Glassy Alloys

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A Zr–Al–Co ternary alloy was investigated in order to clarify the glass-forming ability, thermal stability and mechanical properties. The Zr55Al20Co25 alloy was found to be fabricated in bulk glassy alloy rods with diameters up to at least 2.5 mm. The glassy alloy rod of 2.5 mm in diameter exhibits a large supercooled liquid region of 79 K, followed by a nearly single exothermic peak due to the precipitation of ZrCo + ZrAlCo + ZrAl2Co phases. The glassy alloy rod exhibits Young’s modulus of 114 GPa, high compressive fracture strength of 1900 MPa and total fracture elongation of 1.7%. The finding of forming the bulk glassy alloy at the new ternary composition of Zr55Al20Co25 by the copper mold casting method is encouraging for future search of a new glassy alloy composition.

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1. Introduction

It is well known that bulk glassy alloys have been produced in a number of alloy systems such as lanthanide (Ln)1), Mg–2) Zr–3, 4) Ti–5) Fe–6) Pd–Cu–7) Co–8) Ni–9) Cu–10) and Ca–11) bases for the last one and a half decades. Among these bulk glassy alloy systems, the Zr- and Cu-based alloys exhibit high mechanical strength combined with high ductility and hence have attracted great interest as a new type of bulk structural materials. When we pay attention to Zr-based bulk glassy alloys, the alloy systems can be classified into two groups, i.e., Zr–Al–Ni–Cu13) and Zr–Al–Ni–Cu–(Ti, Nb, Pd)13, 14) systems developed by Sendai group and Zr–Ti–Ni–Cu–Be15) system developed by Caltech group. Very recently, Sendai group has succeeded in developing the third type of Zr-based bulk glassy alloy as presented by Zr–Al–Co and Zr–Al–Fe base systems.15) The new Zr-based alloys have some features of higher Al contents of 10 to 25 at% and higher mechanical strength of 1800 to 1900 MPa which cannot be obtained for the previously reported two kinds of Zr-based bulk glassy alloys. In addition, when the application of Zr-based bulk glassy alloys to biomedical materials is taken into consideration, it is important to develop a new Zr-based bulk glassy alloy without any toxic elements such as Ni and Be. In the previous paper, we have reported that bulk glassy alloy rods in the diameter range up to 5 mm are formed for Zr55Al20Co25Cu4 and the tensile fracture strength reaches 1960 MPa.15) However, little is known about thermal stability of supercooled liquid, solidification behavior and mechanical properties for the new Zr–Al–Co ternary alloys. This information is essential for the evaluation of bulk glass-forming ability as well as for the determination of a more appropriate production method. This paper intends to present the thermal stability of the supercooled liquid including the liquidus temperatures in Zr–Al–Co system and to investigate an optimum alloy composition at which the highest glass-forming ability combined with high mechanical strength is obtained.

2. Experimental Procedure

Ternary alloy ingots with composition of Zr(100−x)−xAl−xCo were prepared by arc melting the mixture of pure Zr, Al and Co metals in an argon atmosphere. The alloy composition represents nominal atomic percentages. Alloy rods with different diameters up to 5 mm were prepared by the copper mold casting method. Alloy ribbons with a cross section of 0.02 × 1.2 mm² were also prepared for comparison by the melt spinning technique. The glassy structure was examined by X-ray diffraction (XRD) and optical microscopy (OM). Thermal stability associated with glass transition, supercooled liquid region and crystallization temperature was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Liquidus temperatures were also measured by differential thermal analysis (DTA) at a low cooling rate of 0.067 K/s. Reduced glass transition temperature was calculated to evaluate the thermal stability of glassy phase. Mechanical properties were measured with an Instron testing machine. The gauge dimension of the testing specimens was 2.5 mm in diameter and 5 mm in height for the compressive deformation mode and the strain rate was 5 × 10⁻⁴ s⁻¹. The fracture surface was examined by scanning electron microscopy (SEM).

3. Results

Figure 1 shows the DSC curves of the melt-spun Zr55Al20Co15−x (x = 12, 16, 20, 24 and 28 at%) glassy alloy ribbons. All the alloys exhibit the sequent transition of glass transition, followed by supercooled liquid region and then crystallization. The glass transition temperature (Tg) remains almost unchanged in the Al content range of 12 to 24 at%, but the crystallization temperature (Tc) increases and shows a maximum value of 838 K for the 20 at% Al alloy, accompanying the change from the distinctly separated two exothermic peaks to a nearly single exothermic peak. With further increasing Al content, the crystallization mode changed again.
to two-stage exothermic reactions.

The similar DSC curves were also obtained for the other alloy series of Zr$_{60}$Al$_{x}$Co$_{40-x}$ and Zr$_{60}$Al$_{x}$Cu$_{40-x}$. Based on the data of these DSC curves, the composition dependence of \(\Delta T_x (= T_x - T_g)\) is shown in Fig. 2. The \(\Delta T_x\) value has a distinct composition dependence. That is, the largest \(\Delta T_x\) of 79 K is obtained for Zr$_{55}$Al$_{20}$Co$_{25}$ and decreases significantly with a deviation of alloy composition from Zr$_{55}$Al$_{20}$Co$_{25}$. The large composition dependence of \(\Delta T_x\) is consistent with the previous data$^{12-14}$ in which no large supercooled liquid region was obtained for Zr$_{60}$Al$_{10}$Co$_{30}$ alloy, though the Zr$_{60}$Al$_{10}$Ni$_{30}$ and Zr$_{60}$Al$_{10}$Cu$_{30}$ glassy alloys exhibit a large supercooled liquid region above 50 K.$^{3,12}$

Figure 3 shows an XRD pattern of the melt-spun Zr$_{55}$Al$_{20}$Co$_{25}$ ribbon annealed at 950 K for 600 s. One can see a number of sharp diffraction peaks indicating the presence of crystalline phases. These phases are identified as a mixed structure of ZrCo, ZrAlCo and Zr$_6$Al$_2$Co, as analyzed in the Fig. 3.

Figure 4 shows the DTA curves of the alloy series Zr$_{55}$Al$_{x}$Co$_{45-x}$. It is seen that the onset temperature of the exothermic peak marked with \(T_l\) decreases significantly with increasing Al content up to 20 at% and then increases with further increasing Al content, leading to a minimum \(T_l\) value for Zr$_{55}$Al$_{20}$Co$_{25}$. Figure 5 shows the composition depen-
dence of $T_g$, $T_l$, and reduced glass transition temperature ($T_g/T_l$) for the Zr$_{55}$Al$_{20}$Co$_{25}$ glassy alloys. The highest $T_g/T_l$ of 0.61 is obtained for Zr$_{55}$Al$_{20}$Co$_{25}$ alloy. Considering the general tendency for glass-forming ability to increase with increasing $T_g/T_l$ which has been recognized for a number of glassy alloys, it is expected that the highest glass-forming ability is obtained at this composition. In addition, bulk glassy alloys have usually been obtained for the alloys with $T_g/T_l$ above 0.60 and hence the Zr$_{55}$Al$_{20}$Co$_{25}$ alloy seems to have a bulk glass-forming ability which enables the formation of a bulk glassy alloy by casting processes. The close correlation between glass-forming ability and $T_g/T_l$ has been interpreted to result from higher stability of liquid phase for the alloys with lower $T_l$ and high viscosity for the alloys with high $T_g$.

We examined the bulk glass-forming ability of the Zr$_{55}$Al$_{20}$Co$_{25}$ alloy by the copper mold casting method. It was confirmed that a glassy single phase is formed in the diameter range up to at least 2.5 mm. Figure 6 shows the DSC curve of the cast Zr$_{55}$Al$_{20}$Co$_{25}$ glassy alloy rod with a diameter of 2.5 mm, together with the data of the corresponding melt-spun glassy alloy ribbon. No distinct difference in the glass transition temperature $T_g$ of the melt-spun glassy ribbon. No distinct difference in the DSC curves is seen in the rod and ribbon samples, indicating the formation of a similar glassy structure for both samples.

The alloy rod of 2.5 mm in diameter exhibited high compressive fracture strength ($\sigma_{c,f}$) of 1900 MPa and Young’s modulus ($E$) of 114 GPa, accompanying the total fracture elongation of 1.7% including elastic elongation of 1.5%. It is noticed that the ($\sigma_{c,f}$) is higher than that (1500–1700 MPa) of previously reported Zr-based bulk glassy alloys. The fracture mode as well as the fracture surface structure agrees well with that for other Zr-based bulk glassy alloys in Zr–Al–Ni–Cu system.

4. Discussion

It was shown that the glassy alloy composition with the largest $\Delta T_g$ is located in the vicinity of Zr$_{55}$Al$_{20}$Co$_{25}$. It is characterized that the Al content is about two times higher than the optimum Al content (about 10 at%) of Zr–Al–Ni and Zr–Al–Cu ternary bulk glassy alloys. Here, we discuss the reason for the significant difference in the optimum Al contents for bulk glass formation. One can notice some significant differences in the equilibrium phase diagrams between Co–Al and Ni–Al or Cu–Al binary systems. That is, the Co-, Ni- and Cu-rich intermetallic compounds in an equilibrium state are CoAl, Ni$_3$Al and Cu$_3$Al phases, respectively. Thus, there is no Co$_3$Al-type equilibrium compound with a low Al content of 25 at%.

5. Summary

We examined the stability of supercooled liquid against crystallization for the alloy series of Zr$_{60}$Al$_x$Co$_{40}$–x, Zr$_{55}$Al$_x$Co$_{45}$–x and Zr$_{50}$Al$_x$Co$_{50}$–x, with the aim of determining an appropriate composition for formation of a bulk glassy alloy in Zr–Al–Co ternary system. The results obtained are
summarized as follows;

(1) The largest supercooled liquid region defined by the difference between \( T_g \) and \( T_x \), \( \Delta T_x (= T_x - T_g) \) was 79 K for Zr\(_{55}\)Al\(_{20}\)Co\(_{25}\) and decreased significantly with deviation of alloy composition.

(2) The glassy alloy crystallizes through a nearly single exothermic peak due to the precipitation of ZrCo + ZrAlCo + Zr\(_6\)Al\(_2\)Co phases.

(3) The largest reduced glass transition temperature defined by \( T_g / T_l \) is 0.61 for Zr\(_{55}\)Al\(_{20}\)Co\(_{25}\) alloy.

(4) The use of the Zr\(_{55}\)Al\(_{20}\)Co\(_{25}\) alloy enabled us to form bulk glassy alloy rods with diameters up to 2.5 mm and the glassy rod of 2.5 mm in diameter exhibits compressive fracture strength of 1900 MPa combined with total fracture elongation of 1.7%.

The formation of the bulk glassy alloy in the simple Zr–Al–Co ternary system provides basic information for future extension to more multi-component systems in which a bulk glassy alloy with much larger maximum sample diameter can be formed by the conventional casting method.

REFERENCES


