New Glassy Zr−Al−Fe and Zr−Al−Co Alloys with a Large Supercooled Liquid Region

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New Zr−Al−Co and Zr−Al−Fe ternary glassy alloys were found to exhibit a large supercooled liquid region above 50 K before crystallization. The largest value of the supercooled liquid region was 64 K for Zr_{55}Al_{20}Co_{25} and 50 K for Zr_{70}Al_{15}Fe_{15}. The highest value of the reduced glass transition temperature (T_g/T_l) was 0.61 for Zr_{55}Al_{20}Co_{25} and 0.60 for Zr_{70}Al_{15}Fe_{15}. The use of the Zr_{55}Al_{20}Co_{25} alloy with the highest T_g/T_l has enabled us to form bulk glassy alloy rods with diameters up to 3 mm by copper mold casting. The Young’s modulus, yield strength, compressive fracture strength, elastic elongation and fracture elongation of the Zr_{55}Al_{20}Co_{25} glassy rod are 92 GPa, 2050 MPa, 2200 MPa, 2.1% and 0.9%, respectively. The distinct plastic elongation indicates that the Zr-based bulk glassy alloy has rather a good ductile nature. The synthesis of the high-strength bulk glassy alloy in the new ternary system is expected to gain a new application field as a new type of bulk glassy alloy.

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1. Introduction

For the last decade, much attention has been paid to bulk glassy alloys because of the importance of scientific and engineering aspects. The motivation for the present global attention to bulk glassy alloys has been attributed to the discoveries of new series of glassy alloys with a large supercooled liquid region before crystallization in Mg–Ln(lanthanide metal)–(Ni, Cu), 1) Ln–Al–(Ni, Cu) 2) and Zr–Al–(Ni, Cu) 3) systems. The low thermal stability of the supercooled liquid against crystallization has enabled us to form bulk glassy alloys by various casting processes. It has subsequently been reported that bulk glassy alloys are also formed in a number of alloy systems, i.e., other Zr-based systems of Zr–Ti–Be–(Ni, Cu) 4) and Zr–(Ti, Nb, Pd)–Al–(Ni, Cu) 5) and Ti–, 6) Hf–, 7) Fe–, 8) Pd–Cu–, 9) Co–, 10) Ni– 11) and Cu– 12) based systems. The high thermal stability of the supercooled liquid against crystallization has enabled us to form bulk glassy alloys by various casting processes. It has subsequently been reported that bulk glassy alloys are also formed in a number of alloy systems, i.e., other Zr-based systems of Zr–Ti–Be–(Ni, Cu) 4) and Zr–(Ti, Nb, Pd)–Al–(Ni, Cu) 5) and Ti–, 6) Hf–, 7) Fe–, 8) Pd–Cu–, 9) Co–, 10) Ni– 11) and Cu– 12) based systems. The lowest critical cooling rate for glass formation is 0.03 K/s for the Pd–Cu–Ni–P system. The maximum sample diameter is approximately 80 mm for the Pd-based system 13) and 30 mm for the Zr-based system. 14) The Zr– and Pd-based bulk glassy alloys have been used as practical materials of sporting goods and electrodes 15–17). In the development history of the Zr-based bulk glassy alloys, their alloy components had been limited to two groups of Zr–Al–(Ni, Cu) including Ti, Nb, Ta or Pd and Zr–Ti–Be–(Ni, Cu). It is important to search for new Zr-based glassy alloys with the high thermal stability of supercooled liquid and to extend bulk glassy alloy systems.

Very recently, we have found that a large supercooled liquid region above 50 K before crystallization is obtained for new Zr-based glassy alloys in Zr–Al–Fe and Zr–Al–Co systems. Further, thermal and mechanical properties of their glassy alloys are investigated.

2. Experimental Procedure

Ternary alloy ingots in Zr−Al–Fe and Zr−Al–Co systems were prepared by arc melting mixtures of pure Zr, Al, Fe and Co metals in an argon atmosphere. Ribbon samples with a cross section of 0.02 × 1.2 mm² were prepared from the alloy ingots by melt spinning. Bulk rod samples with diameters of 1 to 5 mm were also prepared by copper mold casting. The glassy phase was identified by X-ray diffraction and transmission electron microscopy (TEM). The absence of the microscale precipitation phase was also confirmed by optical microscopy (OM). The thermal stability associated with glass transition and crystallization was examined by differential scanning calorimetry (DSC) at the heating rate of 0.67 K/s. The melting and liquid temperatures were measured by differential thermal analysis (DTA) at the heating rate of 0.17 K/s. Mechanical properties in a compressive deformation mode were measured with an Instron testing machine. The gauge dimension was 2 mm in diameter and 4 mm in height and the initial strain rate was 2.4 × 10⁻⁶ s⁻¹. The fracture surface was examined by scanning electron microscopy (SEM). The hardness was measured with a Vickers hardness indenter under the load of 1 kg.

3. Results and Discussion

Figure 1 shows DSC curves of the melt-spun Zr_{85−x}Al_{15}Fe_x
(x = 10, 15 and 20 at%) and Zr_{80−x}Al_{20}Co_x (x = 10, 20,
25 and 30 at%) glassy alloys. A distinct glass transition, followed by a large supercooled liquid region before crystallization is observed for Zr−Al–Fe and Zr−Al–Co ternary glassy alloys. It is noticed that the supercooled liquid region of the 25%Co-containing alloy reaches 64 K which is comparable to those for the Zr−Al–Ni and Zr−Al–Cu alloys 10) developed pre-
Fig. 1 DSC curves of melt-spun Zr$_{85-x}$Al$_{15}$Fe$_x$ and Zr$_{80-x}$Al$_{20}$Co$_x$ glassy alloys.

Fig. 2 Compositional range in which Zr–Al–Co glassy alloys with glass transition are formed by melt spinning, compositional dependence of $T_g$ and $\Delta T_x$ ($= T_x - T_g$), for the Zr–Al–Co ternary glassy alloys. The glass transition is observed in wide composition ranges from 5 to 30 at%Al and from 5 to 50 at%Co. $\Delta T_x$ shows a distinct compositional dependence and the largest $\Delta T_x$ value of 64 K is obtained for Zr$_{55}$Al$_{20}$Co$_{25}$. $\Delta T_x$ larger than 50 K is obtained in the composition range from 20 to 35 at%Co, and it decreases with a deviation of composition from Zr$_{55}$Al$_{20}$Co$_{25}$. Figure 3 shows the changes in the liquidus temperature ($T_l$) and reduced glass transition temperature ($T_g/T_l$) against Co content for the Zr$_{80-x}$Al$_{30}$Co$_x$ ternary glassy alloys. $T_l$ was defined as the offset temperature of an endothermic peak due to melting on the DTA curve. The high $T_g/T_l$ values above 0.6 are obtained in the range from 20 to 27 at%Co and the highest one is 0.61 for Zr$_{55}$Al$_{20}$Co$_{25}$. Based on the compositional dependences of $\Delta T_x$ and $T_g/T_l$ shown in Figs. 2 and 3, we tried to synthesize a bulk glassy alloy by choosing of Zr$_{55}$Al$_{20}$Co$_{25}$.

Figure 4 shows the shape and outer surface of the cast rod samples with diameters of 2 and 3 mm. The outer surface is smooth and no concave due to the precipitation of a crystalline phase is seen. We have also confirmed the absence of a macroscale crystalline phase over the whole transverse cross section of the 3 mm rod sample by OM. However, since a further increase in the rod diameter caused the precipitation of a crystalline phase, the critical diameter for glass formation lied between 3 and 4 mm. Figure 5 shows a compressive stress-elongation curve of the Zr$_{55}$Al$_{20}$Co$_{25}$ rod sample with a diameter of 2 mm. The Young’s modulus defined by the deviation from the linearity is 92 GPa and the elastic elongation limit is 2.1%. The rod sample shows a distinct plastic elongation of 0.9% after yielding, and the yield strength and compressive fracture strength are 2050 and 2200 MPa, respectively. The distinct plastic elongation indicates that the Zr–Al–Co ternary glassy alloy has rather a good ductile nature. The fracture takes place along the maximum shear plane which is declined by about 54 degrees to the direction of applied load and the fracture surface consists of a well-developed vein pattern. It is also noticed that the fracture strength exceeding 2000 MPa is much higher than those (1500 to 1800 MPa) for Zr-based bulk glassy alloys previously reported. The success of synthesizing the bulk glassy alloy with a large supercooled liquid region and good mechanical properties in the new Zr–Al–Co ternary system without Ni is encouraging for a further extension of application fields.
Fig. 3 Changes in the liquidus temperature ($T_l$) and reduced glass transition temperature ($T_g/T_l$) against Co content for melt-spun Zr$_{60-x}$Al$_{20}$Co$_x$ glassy alloys.

Fig. 4 Outer shape and surface morphology of bulk glassy Zr$_{55}$Al$_{20}$Co$_{25}$ alloy rods with diameters of 2 and 3 mm.

3 mm. Considering that bulk glassy alloys in Zr-based systems had been limited to Zr-based alloys containing Ni and/or Cu,\textsuperscript{15–17} the alloy without Ni and Cu is concluded as a new bulk glassy alloy system. It is known that bulk glassy alloys are formed in alloy systems which satisfy the following three empirical rules,\textsuperscript{15, 16} i.e., (1) multicomponent alloys consisting of more than three elements, (2) significant atomic size ratios above 12% among the main constituent elements, and (3) suitable negative heats of mixing among the elements. The atomic size ratio is 1.12 for Zr/Al and 1.14 for Al/Co, which is larger than 12%. In addition, the heats of mixing among constituent elements have negative values of 44 kJ/mol for Zr–Al pair, 41 kJ/mol for Al–Co one and 19 kJ/mol for Zr–Co one. The atomic size ratios and heats of mixing for the Zr–Al–Co system indicate the satisfaction of the criteria described above for the formation of bulk glassy alloys as well as for the stabilization of supercooled liquid. The satisfaction is concluded to result in the formation of bulk glassy alloy with large supercooled liquid region. The mechanism for the stabilization of supercooled liquid for alloys which satisfy the three empirical rules has been described in some previous papers and review.\textsuperscript{15, 16}

4. Summary

We examined the possibility of forming bulk glassy alloys with a high mechanical strength in new Zr-based ternary alloy systems and found new bulk glassy alloys in the Zr–Al–Co system. The large supercooled liquid region above 50 K was obtained in the range of 15 to 25 at%Al and 20 to 35 at%Co. The largest $\Delta T_x$ was given to be 64 K for Zr$_{55}$Al$_{30}$Co$_{25}$. The highest $T_g/T_l$ attained was 0.61 for Zr$_{55}$Al$_{30}$Co$_{25}$ and the use of the alloy composition produced bulk glassy alloy rods with diameters up to 3 mm. The bulk glassy alloy exhibited the Young’s modulus of 92 GPa, high yield strength of 2050 MPa, high compressive fracture strength of 2200 MPa and total fracture elongation of 3.0%. The new Zr-based bulk glassy alloy both with the high glass-forming ability and with the good mechanical properties is expected to be used as a new base alloy system for fundamental researches and applications of bulk glassy alloys.

REFERENCES