Thermal and Mechanical Properties of Cu-Based Cu–Zr–Ti–Y Bulk Glassy Alloys

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A new Cu-based bulk glassy alloy with high tensile fracture strength above 2000 MPa was formed in a $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ alloy by copper mold casting. The maximum sample thickness for glass formation is 4 mm for $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and increases to 5 mm for the 2% Y-containing alloy. The addition of 2% Y also causes an increase in the supercooled liquid region ($\Delta T_x = T_x - T_g$) from 36 to 50 K and in the reduced glass transition temperature (T_g/T_i) from 0.62 to 0.63. The increase in the glass-forming ability (GFA) is presumably due to the increase in ΔT_x and T_g/T_i . The bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ alloy exhibits good mechanical properties, *i.e.*, 1780 MPa for yield strength, 2030 MPa for tensile fracture strength, 2100 MPa for compressive fracture strength, 1.7% for elastic elongation and 1.5% for plastic elongation. The distinct plastic elongation indicates good ductile nature of the Cu-based bulk glassy alloy. The success of synthesizing the new Cu-based bulk glassy alloy with high GFA and good mechanical properties allows us to expect the extension of application fields as a new engineering material.

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1. Introduction

For the last decade, a number of data on the formation and mechanical properties of bulk glassy alloys have been obtained in Zr–Al–TM (TM=Ni, Cu),¹⁾ Zr–(Ti, Nb, Pd)–Al–TM,²⁾ Zr–Ti–Be–TM³⁾ and Pd–Cu–Ni–P⁴⁾ systems because the Zr- and Pd-based bulk glassy alloys possess high mechanical strength and good ductility. As a result, the good mechanical properties combined with high glass-forming ability have enabled us to use the Zr- and Pd-based bulk glassy alloys as practical materials.^{5–8)} For further extension of application fields, it is important to find a new bulk glassy alloy with better mechanical properties and higher glass-forming ability in alloy components with more inexpensiveness, lower melting temperature and higher resistance against oxidation.

Very recently, we have succeeded in finding new Cu-based bulk glassy alloys containing more than 50 at% Cu in Cu–Zr–Ti,⁹⁾ Cu–Hf–Ti,¹⁰⁾ Cu–Zr–Hf–Ti¹¹⁾ and Cu–Zr–Ti–Be¹²⁾ systems. The maximum thickness of these bulk glassy alloys is 4 mm^{9–11)} in the Cu–Zr–Ti, Cu–Hf–Ti and Cu–Zr–Hf–Ti systems and 5 mm¹²⁾ in the Cu–Zr–Ti–Be and Cu–Hf–Ti–Be systems. Moreover, these Cu-based bulk glassy alloys exhibit tensile fracture strength of 2000 to 2500 MPa^{9–12)} which are much higher than those (1500 to 1700 MPa)^{5–8)} for the Zr-based bulk glassy alloys. The increase in the glass-forming ability by the addition of Be has been interpreted¹²⁾ to result from an increase in the degree of the satisfaction of the three empirical rules for the formation of bulk glassy alloys,^{5–7)} *i.e.*, (1) multicomponent system consisting of more than three elements, (2) significant atomic size mismatches above 12% among the main three constituent elements, and (3) suitable negative heats of mixing among the main three elements. Based on the effectiveness of the three empirical rules for the Cu-based alloys,¹²⁾ we have further examined the effect of additional Y element on the glass-forming ability and mechanical properties of the Cu–Zr–Ti and Cu–Hf–Ti glassy

alloys. The additional Y element has much larger atomic size than those for the constituent elements in the Cu-based alloys, though the heats of mixing do not always have negative values against Zr, Hf and Ti. In this case, it is expected that the glass-forming ability and mechanical properties be improved by the addition of a small amount of Y. This paper presents the formation tendency, thermal stability and mechanical properties of the Cu–Zr–Ti–Y bulk glassy alloys. The reason for the effectiveness of Y element on the glass-forming ability is also discussed.

2. Experimental Procedure

Multicomponent alloy ingots with compositions of $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Y}_x$ were prepared by arc melting the mixtures of pure metals in an argon atmosphere. Bulk alloys in rod or sheet form were prepared by the copper mold casting and the melt clamp forging¹³⁾ methods. The diameter of the rod samples was in the range of 2 to 8 mm and the thickness of the sheets was 2 to 5 mm. Ribbon samples with a cross section of $0.03 \times 1.2 \text{ mm}^2$ were also prepared by melt spinning. The structure was examined by X-ray diffraction and transmission electron microscopy (TEM). Thermal stability was evaluated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Solidus and liquidus temperatures were also measured by differential thermal analysis (DTA) at a heating rate of 0.17 K/s. Mechanical properties were measured with an Instron testing machine. The initial strain rate was $5.0 \times 10^{-4} \text{ s}^{-1}$ for tensile tests and $2.5 \times 10^{-3} \text{ s}^{-1}$ for compressive tests. The gauge dimension was 1 mm in thickness, 3 mm in width and 10 mm in length for tensile tests and 2 mm in diameter and 4 mm in height for compressive tests. The tensile and compressive specimens were made from the forged sheet with a thickness of 2 mm and the cast rod with a diameter of 2 mm, respectively. Fracture surface was examined by scanning electron microscopy (SEM). Hardness was measured with a Vickers hardness indenter under a load of 1 kg.

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3. Results

Figure 1 shows DSC curves of the melt-spun $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Y}_x$ ($x = 0, 1, 2$ and 3 at%) glassy alloys. Two exothermic peaks due to crystallization are seen on all the DSC curves and the crystallization process is independent of Y content up to 3 at%. The glass transition temperature (T_g) and crystallization temperature (T_x) tend to decrease from 738 to 667 K and from 774 to 737 K, respectively, with an increase in Y content from 0 to 3 at%. The reduction of T_g is more significant as compared with T_x , leading to an increase in the supercooled liquid region (ΔT_x). In addition, one can see an increase in the difference in the specific heats between glassy solid and supercooled liquid by the addition of 2%Y.

By choosing the 2%Y-containing alloy, we examined the formation tendency of a bulk glassy alloy by the copper mold casting method. Figure 2 shows the outer shape and surface appearance of the cast 2%Y alloy rods with diameters of 4

and 5 mm. Neither voids nor concaves are seen on the outer surface of both the rods. The X-ray diffraction patterns of the cast 2%Y rods are shown in Fig. 3. Only broad peaks are seen and the wave vector of the main broad peak is located at 28.5 nm^{-1} which agrees with that for the melt-spun glassy ribbon. The metallographic and X-ray diffraction data indicate that these bulk rods of 4 and 5 mm in diameter have a single glassy phase. The cooling rate for preparing the glassy rod with a diameter of 5 mm is evaluated to be about 40 K/s ,¹⁴⁾ indicating that glassy alloy can be produced with a cooling rate of above 40 K/s for the present 2%Y-containing alloy. Figure 4 shows DSC curves of the 2%Y glassy rods with diameters of 4 and 5 mm. The sequent transition of glass transition, followed by supercooled liquid region and then two exothermic peaks due to crystallization is the same as that for the melt-spun glassy ribbon shown in Fig. 1. It is concluded that the thermal stability of the 2%Y glassy alloy is independent of sample thickness and cooling rate during sample preparation.

Figure 5 shows stress-elongation curves of the 2%Y

Fig. 1 DSC curves of melt-spun $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Y}_x$ ($x = 1, 2$ and 3 at%) glassy alloys.

Fig. 3 X-ray diffraction patterns of cast $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ alloy rods with diameters of 4 and 5 mm.

Fig. 2 Shape and outer surface appearance of the cast $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ glassy rods with diameters of 4 and 5 mm.

Fig. 4 DSC curves of the cast $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ glassy rods with diameters of 4 and 5 mm.

Fig. 5 Stress-elongation curves under tensile and compressive deformation modes for the cast $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ glassy alloys.

bulk glassy alloy under tensile and compressive deformation modes. The Young's modulus (E), yield strength defined by deviation from the linear relation (σ_y), elastic elongation (ϵ_e), compressive fracture strength ($\sigma_{c,f}$), compressive fracture strength ($\sigma_{c,f}$), compressive plastic elongation (ϵ_p) and tensile fracture strength ($\sigma_{t,f}$) are 115 GPa, 1780 MPa, 1.7%, 2100 MPa, 1.5% and 2030 MPa, respectively. Considering that the E , σ_y , $\sigma_{c,f}$ and $\sigma_{t,f}$ of the 0%Y bulk glassy alloy are 114 GPa, 1785 MPa, 2150 MPa and 2000 MPa, respectively, the addition of 2%Y does not affect significant influence on the mechanical strength of the Cu-based bulk glassy alloy. The fracture under the tensile and compressive deformation modes occurs along the maximum shear plane which is declined by 45 to 55 degrees to the direction of their applied loads and the fracture surface consists of a well-developed vein pattern, as exemplified for the tensile fracture surface in Fig. 6. The feature of the fracture mode agrees with that for other bulk glassy alloys in Zr- and Pd-based systems with good ductility.⁵⁻⁸⁾

4. Discussion

It has previously been reported that bulk glassy alloy alloys are formed at the composition of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and the maximum sample thickness is 4 mm in the case of copper mold casting.^{9,10)} In comparison with the previous data, it is concluded that the maximum sample thickness increases to 5 mm by the addition of 2 at%Y. Here, we discuss the reason for the increase in the glass-forming ability by the addition of 2 at%Y to the Cu-Zr-Ti alloy. It is known that the glass-forming ability is closely related to T_g/T_l and $\Delta T_x (= T_x - T_g)$.^{15,16)} It was shown in Fig. 1 that the ΔT_x increased from 36 K at 0%Y to 50 K at 2 at%Y. We also obtained that the T_g/T_l increases from 0.62 at 0%Y to 0.63 at 2%Y through a significant decrease in T_l from 1173 to 1122 K. These data indicate that the previous relation between glass-forming ability and ΔT_x or T_g/T_l is also satisfied for the present Cu-Zr-Ti-Y glassy

Fig. 6 Fracture surface appearance of the cast $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ glassy sheet subjected to tensile fracture.

alloy.

Next, we discuss the reason why the addition of 2%Y causes an increase in the thermal stability of the supercooled liquid against crystallization which is demonstrated by the increase in ΔT_x and T_g/T_l . The high glass-forming ability leading to the formation of a bulk glassy alloy as well as the stabilization of the supercooled liquid region has been recognized to be achieved in the alloys which satisfy the following three empirical rules,^{5–7) i.e.,} (1) multicomponent system consisting of more than three elements, (2) significant atomic mismatches above 12% among the main three constituent elements, and (3) suitable negative heats of mixing among the main elements. The atomic size ratios are 1.14 for Y/Zr, 1.23 for Y/Ti, 1.09 for Zr/Ti, 1.25 for Zr/Cu and 1.15 for Ti/Cu.¹⁷⁾ In addition, the heats of mixing for Cu–Y, Zr–Y and Ti–Y are –22, 0 and –15 kJ/mol,¹⁸⁾ respectively. It is clear that the addition of Y to Cu–Zr–Ti alloy causes an increase in the degree of the satisfaction of the three empirical rules as compared with the Cu–Zr–Ti ternary alloy. The increase is concluded to result in an increase in glass-forming ability through the increases in ΔT_x and T_g/T_l . It was also pointed out in Fig. 1 that the difference in the specific heats between the glassy solid and the supercooled liquid increases significantly by the addition of 2 at%Y. The increase in the difference in the specific heats corresponds to the decrease in the difference in the Gibbs free energy between the glassy and supercooled liquid. The smaller free energy also implies that the driving force from supercooled liquid to crystalline phase is low as is the case for that from glassy solid to crystalline phase.

5. Summary

Bulk glassy alloys of 5 mm in diameter were formed in a $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Y}_2$ alloy by the copper mold casting method. The maximum diameter for the $\text{Zu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ ternary alloy is 4 mm and hence the addition of 2 at%Y is effective for an increase in glass-forming ability. It is also confirmed

that the ΔT_x and T_g/T_l increase from 36 to 50 K and from 0.62 to 0.63, respectively, by the addition of 2%Y. The increases in the ΔT_x and T_g/T_l are closely related to the increase in glass-forming ability. The bulk glassy alloys exhibit good mechanical properties, i.e., E of 115 GPa, σ_y of 1780 MPa, ε_e of 1.7%, $\sigma_{t,f}$ of 2030 MPa, $\sigma_{c,f}$ of 2100 MPa and ε_p of 1.5%. The combination of high GFA and good mechanical properties for the new Cu–Zr–Ti–Y bulk glassy alloy is encouraging for the future development of bulk glassy alloy as a new type of engineering material.

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