Formation, Thermal Stability and Mechanical Properties of Cu-Zr and Cu-Hf Binary Glassy Alloy Rods

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Glassy alloy rods with diameters up to 1.5 mm exhibiting a large supercooled liquid region before crystallization and high mechanical strength were formed in Cu-Zr and Cu-Hf binary alloy systems by the copper mold casting method. The large supercooled liquid region exceeding 40 K was obtained in the composition range of 30 to 70 at%Zr and 35 to 60 at%Hf. The largest value of the supercooled liquid region defined by the difference between glass transition temperature (T_g) and crystallization temperature (T_x), $\Delta T_x (= T_x - T_g)$, was 58 K for Cu₆₀Zr₄₀ and 59 K for Cu₅₅Hf₄₅. The reduced glass transition temperature (T_g/T_i) of the two alloys was 0.61 and 0.59, respectively. The alloys with large ΔT_x above 50 K were formed into a bulk glassy alloy form with diameters up to 1.5 mm by copper mold casting. The Cu₆₀Zr₄₀, Cu₄₅Zr₅₅, Cu₆₀Hf₄₀ and Cu₅₅Hf₄₅ glassy alloy rods exhibited high fracture strength of 1920, 1880, 2245 and 2260 MPa, respectively, Young's modulus of 107, 102, 120 and 121 GPa, respectively, a nearly constant elastic elongation of about 1.9% and plastic elongation up to 2.2%. The formation of these binary glassy alloy rods can be interpreted in the framework of the concept of the formation of the unique glassy structure consisting mainly of icosahedral atomic configuration as similar to that for special multi-component alloys with the three component rules.

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1. Introduction

Since the first syntheses of bulk glassy alloys in metal-metal type alloy systems without metalloid such as Mg-,¹⁾ La-²⁾ and Zr-³⁾ based systems for several years from 1988 to 1990, a large number of bulk glassy alloys have been formed for particular multi-component alloy systems.⁴⁻⁶⁾ It has been pointed out that these bulk glassy alloys have the following three component rules,^{4,5)} i.e., (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches above 12%, and (3) negative heats of mixing. However, it has recently been reported^{7,8)} that bulk glassy alloys are formed in Cu-Zr-Ti and Cu-Hf-Ti ternary and Cu-Zr and Cu-Hf binary systems where the three component rules are not satisfied. The maximum diameter of the glassy single phase alloy is less than about 1.5 mm and the further increase in the sample diameter causes a mixed structure of glassy phase containing nanoscale particles with a size of about 5 nm in Cu-Zr-Ti and Cu-Hf-Ti systems.⁹⁻¹¹⁾ In addition, it has been pointed out that the structure of the bulk glassy alloys with the three component rules consists mainly of short-range icosahedral atomic configuration.^{12,13)} The formation of the glassy phase in the Cu-Zr-Ti and Cu-Zr-Ti-(Ni or Co) alloys is thought to have a close relation to the Cu₁₀Zr₇ phase with a complex orthorhombic structure.^{14,15)} The complex orthorhombic structure has been presumed to be the origin for the formation of an icosahedral phase in the crystallization process of Cu-Zr-Ti-(Pd or Au) glassy alloy.^{16,17)} These recent results also suggest that the short-range icosahedral atomic configuration plays a dominant role in the formation of bulk glassy alloys as well as the stability of supercooled liquid against crystallization. This concept is also supported from the result that the icosahedral phase precipitates as a primary crystallization phase in Zr₇₀Cu₂₉Pd₁ alloy.¹⁸⁾ With the aim of confirming appropriateness of our concept, we have examined in more details the formation of

Cu-Zr and Cu-Hf bulk glassy alloys, though the formation of Cu-Zr binary bulk glassy alloys has already been mentioned two years ago.^{7,8)} This paper intends to present the formation, thermal stability and mechanical properties of bulk glassy alloys in Cu-Zr and Cu-Hf binary systems and to discuss the reason for the formation of these new bulk glassy alloys on the basis of the importance of the short-range icosahedral atomic configuration.

2. Experimental Procedure

Binary Cu-based alloy ingots with compositions of Cu_{100-x}Zr_x and Cu_{100-x}Hf_x were prepared by arc melting the mixtures of pure Cu (99.99 mass%), Zr (99.9 mass%) and Hf (99.9 mass%) metals in an argon atmosphere. The alloy compositions represent the nominal atomic percentages. Cylindrical rod alloys of about 50 mm in length and 1 to 3 mm in diameter were produced by a copper mold casting method. Ribbon samples with a cross section of 0.02 × 1.2 mm² were also produced by the melt spinning method. Glassy structure was examined by X-ray diffraction and the absence of micro-scale crystalline phase was confirmed by optical microscopy (OM). Thermal stability associated with glass transition, supercooled liquid region and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The melting and liquidus temperatures were measured with a differential thermal analyzer (DTA) at a heating rate of 0.17 K/s. Mechanical properties in a compressive deformation mode were measured with an Instron testing machine. The test specimen had a diameter of 1.0 or 1.5 mm and a height of 2.0 or 3.0 mm, respectively, and the initial strain rate was fixed to be 5 × 10⁻⁴ s⁻¹. Fracture surface was examined by scanning electron microscopy (SEM).

Fig. 1 X-ray diffraction patterns of $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rods with diameters of 1.0 and 1.5 mm.

3. Results

Figure 1 shows X-ray diffraction patterns of $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rods with diameters of 1.0 and 1.5 mm. Only broad peaks are seen in the diffraction patterns, indicating that a glassy phase without crystalline phase is formed even for the Cu-Zr and Cu-Hf binary alloy rods. With the aim of confirming the formation of nearly the same glassy phase as that for the melt-spun glassy alloy ribbons, DSC curves of the $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rods are shown in Fig. 2. The data of the melt-spun glassy alloy ribbons are also shown for comparison. The T_g and T_x are 733 K and 791 K, respectively, for the $\text{Cu}_{60}\text{Zr}_{40}$ alloy rod, 669 K and 719 K, respectively, for the $\text{Cu}_{45}\text{Zr}_{55}$ alloy rod, 773 K and 827 K, respectively, for the $\text{Cu}_{60}\text{Hf}_{40}$ alloy rod and 771 K and 830 K, respectively, for the $\text{Cu}_{55}\text{Hf}_{45}$ alloy rod, being nearly the same as those for the $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy ribbons. The liquidus temperature (T_l) was measured as 1198 K for $\text{Cu}_{60}\text{Zr}_{40}$, 1206 K for $\text{Cu}_{45}\text{Zr}_{55}$, 1290 K for $\text{Cu}_{60}\text{Hf}_{40}$ and 1295 K for $\text{Cu}_{55}\text{Hf}_{45}$ and hence T_g/T_l values of their alloys were evaluated as 0.61, 0.56, 0.60 and 0.59, respectively. These T_g/T_l values indicate that the three binary alloys have high glass-forming ability leading to the formation of bulk glassy alloy rods by the copper mold casting method.

Figure 3 shows nominal compressive stress-strain curves of the $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rods. The Young's modulus (E), fracture strength (σ_f) and plastic elongation ($\varepsilon_{c,p}$) are 107 GPa, 1920 MPa and 0.2%, respectively, for the $\text{Cu}_{60}\text{Zr}_{40}$ alloy rod, 102 GPa, 1880 MPa and 1.5%, respectively, for the $\text{Cu}_{45}\text{Zr}_{55}$ alloy rod, 120 GPa, 2245 MPa and 0.4%, respectively, for the $\text{Cu}_{60}\text{Hf}_{40}$ alloy rod and 121 GPa, 2260 MPa and 2.2%, respectively, for the $\text{Cu}_{55}\text{Hf}_{45}$ alloy rod. Furthermore, it is noticed that the $\text{Cu}_{45}\text{Zr}_{55}$ and $\text{Cu}_{55}\text{Hf}_{45}$ alloy rods exhibit distinct plastic

Fig. 2 DSC curves of $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rods with diameters of 1.0 and 1.5 mm. The data of the corresponding melt-spun glassy alloy ribbons are also shown for comparison.

Fig. 3 Compressive stress-strain curves of $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rods with diameters of 1.0 and 1.5 mm.

elongation of 1.5 to 2.2%. It has previously been reported that the E and σ_f are 112 GPa and 2150 MPa, respectively, for the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ alloy rod,⁷⁾ 115 GPa and 2210 MPa, respectively, for the $\text{Cu}_{55}\text{Zr}_{40}\text{Al}_5$ alloy rod,¹⁹⁾ 124 GPa and 2160 MPa, respectively, for the $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloy rod^{7,8)} and 128 GPa and 2370 MPa, respectively, for the $\text{Cu}_{50}\text{Hf}_{42.5}\text{Al}_{7.5}$ alloy rod.²⁰⁾ The much higher values of E and σ_f for the $\text{Cu}_{60}\text{Hf}_{40}$ and $\text{Cu}_{55}\text{Hf}_{45}$ alloy rods as compared with $\text{Cu}_{60}\text{Zr}_{40}$ and $\text{Cu}_{45}\text{Zr}_{55}$ alloy rods are consistent with the previous data on the Cu-based ternary glassy alloy rods. The higher E and σ_f values for the Cu-Hf alloy rods also correspond to the result that T_g values are considerably higher for Cu-Hf glassy alloys than for Cu-Zr glassy alloys. It

Fig. 4 Fracture surface morphology of $\text{Cu}_{45}\text{Zr}_{55}$ (a, b) and $\text{Cu}_{55}\text{Hf}_{45}$ (c, d) glassy alloy rods fractured in a uniaxial compressive deformation mode.

is well known²¹⁾ that T_g reflects the binding force among the constituent elements. Figure 4 shows the fracture surface morphology of the $\text{Cu}_{45}\text{Zr}_{55}$ and $\text{Cu}_{55}\text{Hf}_{45}$ alloy rods. The fracture occurs along the maximum shear stress plane which is declined by about 45 degrees to the direction of compressive applied load. In addition, the fracture surface consist mainly of vein pattern elongated to the direction of shear sliding. These deformation and fracture behavior indicate that the $\text{Cu}_{55}\text{Hf}_{45}$ glassy alloy rod has the best mechanical properties in the binary glassy alloy rods, as is evidenced from the high fracture strength of 2260 MPa combined with a large plastic elongation of 2.2%.

4. Discussion

We discuss the reason why the bulk glassy alloys are formed in Cu-Zr and Cu-Hf binary alloy systems by the copper mold casting method. It was shown that binary bulk glassy alloys are formed in $\text{Cu}_{45}\text{Zr}_{55}$ and $\text{Cu}_{60}\text{Zr}_{40}$ glassy alloy rods in the diameter range up to 1.5 mm, even though bulk glassy alloys with diameters up to about 10 mm are formed in Zr-rich Zr-Cu-Al ternary system.²²⁾ We have also reported that the addition of a small amount (1 to 5 at%) of Pd to $\text{Cu}_{30}\text{Zr}_{70}$ ¹⁸⁾ and $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ ¹⁶⁾ alloys causes the precipitation of an icosahedral phase as a primary crystallization phase. The icosahedral phase has a very fine particle size of 3 to 50 nm and precipitates very homogeneously in the glassy matrix. In addition, we have examined the radial distribution

function of the $\text{Cu}_{30}\text{Zr}_{70}$ glassy alloy. The coordination numbers around Cu and Zr atoms agree with those expected from the nominal atomic component, indicating the absence of appreciable segregation of the constituent elements. In these previous papers, it has also been pointed out that the homogeneous precipitation of the icosahedral phase as the primary crystallization phase originates from the unique glassy structure consisting mainly of short-range icosahedral atomic configuration. Furthermore, the metal-metal type alloys with the three component rules as exemplified for Zr-Al-Cu and Zr-Al-Ni systems have a unique structure with the features of (1) highly dense packed atomic configurations, (2) new local atomic configurations, and (3) long-range homogeneity with attractive interaction, being consistent with the formation of short-range icosahedral atomic configuration.⁵⁾ Based on these previous data, it may be concluded that the Cu-Zr binary alloys have a short-range icosahedral atomic configuration which is different from those of the corresponding equilibrium compounds,²³⁾ as similar to that for the Zr-Al-Ni and Zr-Al-Cu bulk glassy alloys.⁵⁾ This is thought to result in the high glass-forming ability through the achievement of high stability of supercooled liquid against crystallization even for the Cu-Zr and Cu-Hf binary alloys.

5. Summary

Bulk glassy alloys were formed in the diameter range up to 1.5 mm in Cu-Zr and Cu-Hf binary systems by the copper mold casting method. The T_g , ΔT_x and T_g/T_l are 733 K, 58 K and 0.61, respectively, for the $\text{Cu}_{60}\text{Zr}_{40}$ glassy alloy rod and 669 K, 50 K and 0.56, respectively, for the $\text{Cu}_{45}\text{Zr}_{55}$ glassy alloy rod, and 773 K, 54 K and 0.60, respectively, for the $\text{Cu}_{60}\text{Hf}_{40}$ alloy rod and 771 K, 59 K and 0.59, respectively, for the $\text{Cu}_{55}\text{Hf}_{45}$ alloy rod. No distinct difference in the thermal stability between the cast glassy alloy rods and the melt-spun glassy alloy ribbons was recognized. The E , σ_f and ε_e are 107 GPa, 1920 MPa and 0.2%, respectively, for the $\text{Cu}_{60}\text{Zr}_{40}$ alloy rod, 102 GPa, 1880 MPa and 1.5%, respectively, for the $\text{Cu}_{45}\text{Zr}_{55}$ alloy rod, 120 GPa, 2245 MPa and 0.4%, respectively, for the $\text{Cu}_{60}\text{Hf}_{40}$ alloy rod and 121 GPa, 2260 MPa and 2.2%, respectively, for the $\text{Cu}_{55}\text{Hf}_{45}$ alloy rod.

The fracture occurred along the shear stress plane which was declined by about 45 degrees to the direction of applied load and the fracture surface consisted mainly of vein pattern elongated to the shear sliding direction. The formation of the Cu-Zr and Cu-Hf binary glassy alloys is presumably due to the high thermal stability of supercooled liquid against crystallization through the unique atomic configuration which is different from that of the corresponding crystalline phases.

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