Synthesis and Fundamental Properties of Cu-Based Bulk Glassy Alloys in Binary and Multi-component Systems

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A glassy phase containing cubic phase particles with a size of 3–5 nm was formed in cast Cu₆₀Zr₃₀Ti₁₀ and Cu₆₀Hf₃₀Ti₁₀ bulk alloys. The cubic phase is in a metastable state and its lattice parameter (a_0) is 0.45 nm for the former alloy and 0.51 nm for the latter. These bulk alloys exhibit good mechanical properties of 2000–2130 MPa for tensile strength ($\sigma_{t,f}$), 2060–2160 MPa for compressive strength ($\sigma_{c,f}$) and 0.008–0.017 for compressive plastic strain ($\epsilon_{c,p}$). The temperature interval of the supercooled liquid (SL) region prior to crystallization is 37 K for Cu₆₀Zr₃₀Ti₁₀ and 67 K for Cu₆₀Hf₃₀Ti₁₀. The primary crystallization occurred by precipitation of cubic CuZr ($a_0 = 0.35$ nm) in a diffusion-controlled growth mode of nuclei and an orthorhombic Cu₈Hf₃ phase in an interface diffusion-controlled growth of nuclei with decreasing nucleation rate. The difference in the precipitation modes is interpreted to be the origin of the difference in the SL region. Furthermore, the addition of Al to Cu–Zr and Cu–Hf alloys caused the formation of a glassy single phase in the rod form with diameters up to at least 3 mm, though bulk glassy alloy rods with critical diameters up to 1.5 mm and $\sigma_{c,f}$ of 1920–2260 MPa were formed in Cu–Zr and Cu–Hf binary systems. The ternary bulk glassy alloys exhibited high $\sigma_{c,f}$ of 2100–2370 MPa with $\epsilon_{c,p}$ of 0.002–0.006. The addition of Pd, Pt, Ag or Au increased ΔT_x and a large ΔT_x of 102–110 K was obtained for the Cu–Hf–Al–M (M=Pd or Ag) glassy alloys. The synthesis of Cu-based bulk glassy alloys with good mechanical properties and large ΔT_x in glassy single, and mixed glassy and cubic phase states, is important for future applications of bulk glassy alloys.

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1. Introduction

It is known that high-strength bulk glassy alloys are obtained in Zr- and Pd-based alloy systems by the copper mold casting and water quenching techniques.^{1–4)} It is important to develop a new bulk glassy alloy with high strength and good ductility in late transition-metal based alloys such as Fe-, Co-, Ni- and Cu-based systems because they are expected to have much higher mechanical strength. A number of bulk glassy alloys developed to date include Cu as one of the major solute elements, as exemplified by Zr–Al–Cu, Zr–Al–Ni–Cu, Zr–Ti–Ni–Cu–Be and Ti–Zr–Ni–Cu–Sn glassy alloys.^{1–4)} Subsequently, some bulk glassy alloys containing a large amount of Cu (40 to 45 at%) have also been developed.⁵⁾ However, no data have been available on the formation of Cu-based bulk glassy alloys with more than 50 at%Cu. In 2000, Inoue *et al.* succeeded for the first time in synthesizing Cu-based bulk glassy alloys in Cu–Zr–Ti,^{6,7)} Cu–Zr,^{7,8)} Cu–Hf–Ti,^{7,9)} Cu–Hf^{7,8)} and Cu–Zr–Hf–Ti¹⁰⁾ systems. It has been reported that glassy alloy rods with diameters up to 1.5 mm are formed even in Cu–Zr and Cu–Hf binary alloy systems. Multi-component Cu-based bulk glassy alloys have been prepared in diameters up to 4 mm, and exhibited high fracture strength of 2000–2160 MPa as well as significant plastic strain of 0.008 to 0.017,^{6–8,10)} much larger than observed in other bulk glassy alloys.^{1–4)} Subsequent study has demonstrated that the Cu-based bulk glassy alloys exhibiting good mechanical properties consist of a glassy phase containing high volume fractions of metastable cubic phase with a size of 3–5 nm.^{11,12)} Thus, the new Cu-based glassy alloys in Cu–Zr–Ti and Cu–Hf–Ti systems are classified as a new type of nanocrystal-dispersed bulk glassy alloy. Cu-based bulk glassy alloys without any second phase have also been synthesized in Cu–Zr–Al and Cu–Hf–Al based systems.

This paper aims to review our recent results on the formation, thermal stability, mechanical properties and corrosion resistance of bulk glassy single phase alloys and nanocrystal-dispersed glassy alloys in Cu-based binary and multi-component systems in which Cu exceeds 50 at%.

2. Formation and Properties of Binary Bulk Glassy Alloys

Figure 1 shows X-ray diffraction patterns of Cu₆₀Zr₄₀, Cu₄₅Zr₅₅, Cu₆₀Hf₄₀ and Cu₅₅Hf₄₅ glassy alloy rods with

Fig. 1 X-ray diffraction patterns of Cu₆₀Zr₄₀, Cu₄₅Zr₅₅, Cu₆₀Hf₄₀ and Cu₅₅Hf₄₅ glassy alloy rods with diameters of 1.0 and 1.5 mm.

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.

diameters of 1.0 and 1.5 mm produced by the copper mold casting method.⁸⁾ 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 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 for 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, for the $\text{Cu}_{45}\text{Zr}_{55}$ alloy rod, 773 K and 827 K, for the $\text{Cu}_{60}\text{Hf}_{40}$ alloy rod and 771 K and 830 K, for the $\text{Cu}_{55}\text{Hf}_{45}$ alloy rod, nearly the same as those for $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{60}\text{Hf}_{40}$ 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 the T_g/T_l values of their alloys were 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.⁸⁾ The Young's modulus (E), fracture strength (σ_f) and plastic elongation ($\epsilon_{c,p}$) 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%, for the $\text{Cu}_{45}\text{Zr}_{55}$ alloy rod, 120 GPa, 2245 MPa and 0.4%, for the $\text{Cu}_{60}\text{Hf}_{40}$ alloy rod and 121 GPa, 2260 MPa and 2.2%, for the $\text{Cu}_{55}\text{Hf}_{45}$ alloy rod. Furthermore,

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.

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.

it was observed that the $\text{Cu}_{45}\text{Zr}_{55}$ and $\text{Cu}_{55}\text{Hf}_{45}$ alloy rods exhibit distinct plastic elongation of 1.5–2.2%. 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 inclined by about 45 degrees to the direction of compressive applied load. In addition, the fracture surface consists mainly of vein patterns elongated in the direction of shear sliding. These deformation and fracture behaviors indicate that the Cu-Zr and Cu-Hf glassy alloy rods have good mechanical properties combined with fracture strength over 2000 MPa and distinct plastic elongation.

It has been reported that the addition of 1–5 at%Pd to $\text{Cu}_{30}\text{Zr}_{70}$ ¹³⁾ and $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ ¹⁴⁾ causes the precipitation of an icosahedral phase as a primary crystallization phase. The icosahedral phase has a fine particle size of 3–50 nm and precipitates very homogeneously in the glassy matrix. In addition, we have confirmed the absence of any appreciable segregation of elemental Cu and Zr at the first neighboring position in the radial distribution function (RDF) profile of $\text{Cu}_{30}\text{Zr}_{70}$ glassy alloy.¹⁵⁾ That is, the local atomic configuration is different from those for the corresponding equilibrium compounds. These earlier data have been interpreted on the assumption that the Cu-based glassy alloys have a unique glassy structure consisting mainly of short-range icosahedral atomic configurations. Furthermore, the melt-metal type alloys with three component rules such as Zr-Cu-Al and Zr-Ni-Al systems have an unique structure with the features of (1) highly dense-packed atomic configuration, (2) new local atomic configuration, and (3) long-range homogeneity with attractive interaction,⁴⁾ being consistent with the formation of a short-range icosahedral atomic configuration. Based on these earlier data, it may be also concluded that the high glass-forming ability of the Cu-Zr binary alloys originates from the formation of a unique local atomic configuration such as an icosahedral atomic configuration which is different from the local structure of the corresponding equilibrium compounds. It is well known that the icosahedral type short-range atomic configuration is one of the favorable glassy structures leading to enhancement of stability of the supercooled liquid against crystallization.¹³⁾

3. Formation and Thermal Stability of Multi-component Bulk Glass Alloys

Figure 5 shows X-ray diffraction patterns of Cu-Zr-Ti and

Fig. 5 X-ray diffraction patterns of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$ glassy alloy rods with diameters of 3 and 4 mm produced by copper mold casting. The data of the melt-spun glassy alloy ribbons are also shown for comparison.

Cu-Hf-Ti alloy rods with diameters of 3 and 4 mm prepared by copper mold casting, together with data of melt-spun alloy ribbons. All the alloy rods have a broad peak without any crystalline peaks, indicating the formation of predominantly a single glassy phase. Their glassy alloy rods have a smooth outer surface without the concavities and ruggedness that would result from the precipitation of a crystalline phase, and show good metallic luster. The Cu-based ternary alloys in $\text{Cu}_{60}\text{Zr}_{40-x}\text{Ti}_x$ and $\text{Cu}_{60}\text{Hf}_{40-x}\text{Ti}_x$ systems have T_g/T_l above 0.60 over a wide range of compositions from 0–25 at%Ti. The maximum values (0.63) of T_g/T_l in the vicinity of 20 at%Ti are due to the decrease in T_l . Figure 6 shows DSC curves of the $\text{Cu}_{60}\text{Zr}_{40-x}\text{Ti}_x$ and $\text{Cu}_{60}\text{Hf}_{40-x}\text{Ti}_x$ glassy alloys,

Fig. 6 Differential scanning calorimetric (DSC) curves of $\text{Cu}_{60}\text{Zr}_{40-x}\text{Ti}_x$ (a) and $\text{Cu}_{60}\text{Hf}_{40-x}\text{Ti}_x$ (b) ($x = 0$ to 40 at%) glassy alloys.

Fig. 7 Nominal stress-strain curves of cast $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$ glassy alloy rods. (a) compressive deformation mode, and (b) tensile deformation mode.

respectively. It can be seen that the Cu-Zr-Ti alloys with high glass-forming ability do not show a large supercooled liquid region prior to crystallization, though the Cu-Hf-Ti alloys exhibit a rather large supercooled liquid region from 28–78 K. In addition, the Cu-Zr-Ti glassy alloys crystallize through multiple states, suggesting that the primary crystallization phase is in a metastable state. The strange phenomenon that the alloys without a large supercooled liquid region before crystallization exhibit a high glass-forming ability is investigated in more details later.

4. Mechanical Properties and Corrosion Resistance

The Cu-based glassy alloy rods exhibited good mechanical properties which have not been obtained in Zr-, Mg- and lanthanide(Ln)-based bulk glassy alloys.^{1–4)} The Young's modulus (E), yield strength (σ_y), $\sigma_{t,f}$, $\sigma_{c,f}$ and $\varepsilon_{c,p}$ are 114 GPa, 1785 MPa, 2000 MPa, 2150 MPa and 0.012, respectively, for $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and 124 GPa, 2040 MPa, 2130 MPa, 2160 MPa and 0.017, for $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$, as shown in Fig. 7. We have also reported that the addition of Be to Cu-Zr-Ti alloy ($\text{Cu}_{54}\text{Zr}_{27}\text{Ti}_9\text{Be}_{10}$) causes a further increase in the E , σ_y , $\sigma_{t,f}$ and $\sigma_{c,f}$ to 146 GPa, 2180 MPa, 2450 MPa and 2500 MPa, respectively, in conjunction with rather good plastic strain of 0.035 under a compressive applied load.¹⁶⁾ Although the supercooled liquid region defined by the difference between T_g and T_x , $\Delta T_x (= T_x - T_g)$, is as small as 37 K for $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$, the addition of Ni or Co increases ΔT_x to 60 K for $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{95}\text{Ni}_5$ and 49 K for $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{96}\text{Co}_4$.¹⁷⁾ The 5%Ni- and 4%Co-containing alloys also maintain high yield strength of about 1900 MPa. We further examined the effect of Nb on the mechanical properties of Cu-Zr-Ti-Nb glassy alloys.¹⁸⁾ The yield strength increases with increasing Nb content and the highest yield strength is 2050 MPa for $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{91}\text{Ni}_5\text{Nb}_4$ alloy rod. The Cu-Zr-Ti-Nb glassy alloys exhibit good corrosion resistance in various chemical aqueous solutions such as 1NHCl, 3%NaCl and 1NH₂SO₄ + 0.001NNaCl.¹⁹⁾ It has been clarified that the improvement of corrosion resistance by the addition of Nb is mainly due to an increase in

corrosion potential rather than a decrease in current density. Furthermore, we examined the change in cationic concentration of M (M = Cu, Zr and Ti) in the surface of the film containing Nb.¹⁹⁾ With increasing Nb content, the cationic concentrations of Zr, Ti and Nb in the surface film increase, while the Cu concentration decreases in comparison with each nominal concentration. These experimental data indicate that enrichment with Zr, Ti and Nb plays a dominant role in the enhancement of corrosion resistance.

5. Formation and Microstructure of Bulk Nanocrystal-Dispersed Glassy Alloys

We examined the crystallization behavior of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ glassy alloys.^{12,20)} The ΔT_x was 37 K for the former alloy and 67 K for the latter, as shown in Fig. 6. The ordinary X-ray diffraction patterns showed a broad peak without any crystalline peak.²⁰⁾ In addition, the ordinary radial distribution function showed a broad peak at the first nearest neighbor position for both alloys. However, as is evident from the environmental RDF curves around Cu and Zr atoms for the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ glassy alloy shown in Fig. 8, the RDF curve around Cu consists of a broad peak at the first neighboring position, while the curve around Zr separates to two peaks consisting of Zr-Cu and Zr-Zr atomic pairs. This result indicates that elemental Zr and Cu are separated at the first neighboring position in the as-spun glassy phase. With the aim of clarifying the separated glassy structure, high-resolution TEM images and selected-area electron diffraction patterns of the as-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloys are shown in Fig. 9.¹²⁾ Very fine fringe-contrast regions with a size of about 5 nm are homogeneously dispersed in an isolated fashion in the glassy matrix and there is no appreciable difference in the dispersion nanostructures of the two alloys. Figure 10 shows the nanobeam electron diffraction patterns of the fringe contrast regions and their analytical results. All the reflection spots are analyzed as a cubic phase and its lattice parameter is 0.45 nm for the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ alloy and 0.51 nm for the $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloy. The HAADF-STEM images of the two as-spun alloys are

Fig. 8 Environmental radial distribution function (RDF) curves around Cu (a) and Zr (b) atoms for $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ glassy alloys.

Fig. 10 Nanobeam diffraction patterns of the fringe contrast regions in as-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ (a, b) and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ (c, d) glassy alloys.

Fig. 9 High resolution TEM images and selected-area electron diffraction patterns of as-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ (a, b) and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ (c, d) glassy alloys.

shown in Fig. 11.²¹⁾ The bright contrast region with a size of 3–5 nm disperses homogeneously. Considering that the bright- and dark-contrast regions correspond to Zr-rich and Cu-rich regions, respectively, it is concluded that the as-spun

alloys consist of a modulated structure consisting of Zr- and Cu-rich regions. The Guinier plot of small angle X-ray scattering data of the as-spun $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloy has also indicated that the size of the modulated regions is approx-

Fig. 11 HAADF-STEM images of as-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ (a) and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ (b) glassy alloys.

Table 1 Nanobeam EDX results of the melt-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ (a) and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ (b) alloys. (in at%).

	(a)			(b)		
	Cu	Zr	Ti	Cu	Hf	Ti
Nanocrystal	67.7	26.5	5.8	68.8	26.8	4.4
	71.2	23.5	5.3	64.9	28.7	6.4
	70.9	24.4	4.7	69.0	25.5	5.5
	65.7	28.3	6.0	64.4	29.8	5.8
Average	68.1	26.0	5.9	70.1	25.4	4.5
	68.8	25.7	5.5	67.5	27.2	5.3
	59.3	33.0	7.7	52.7	38.9	8.4
Glass	51.2	39.6	9.2	49.5	41.2	9.3
	54.6	36.9	8.5	53.6	39.7	6.7
	55.0	37.0	8.0	41.7	48.4	9.9
	60.4	31.5	8.1	42.3	48.2	9.5
Average	56.1	35.6	8.3	48.0	43.2	8.8
Whole area (diameter 1 μm)	61.4	30.3	8.3	62.8	29.8	7.4

imately 3–4 nm.²¹⁾ In addition, we analyzed alloy compositions of their modulated regions with Zr- and Cu-rich compositions by nanobeam energy dispersion X-ray spectroscopy.²¹⁾ Table 1 summarizes the analytical alloy compositions of the fringe contrast (nanocrystal) region and the glassy regions for the as-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloys. The nanocrystalline phase has a Cu-rich, Zr-(or Hf)-poor and Ti-poor composition in comparison with the nominal alloy composition, while the glassy phase has a Cu-poor, Zr-(or Hf)-rich and Ti-rich composition. It is therefore concluded that the bright contrast region with Zr- or Hf-rich composition corresponds to the glassy region and the dark contrast region with a Cu-rich composition consists of the nanocrystalline phase.

6. Crystallization Behavior of Bulk Nanocrystal-Dispersed Glassy Alloys

It was shown that the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloys in as-spun and as-cast states had a nanoscale mixed structure consisting of a cubic phase with a size of 3–5 nm

embedded in a glassy matrix. The cubic phase has a lattice parameter of 0.45 nm for the former alloy and 0.51 nm for the latter, and a relatively Cu-rich composition in comparison with the nominal composition. Figure 12 shows X-ray diffraction patterns of the Cu-Zr-Ti and Cu-Hf-Ti alloys annealed at temperatures just above the first exothermic peak.²²⁾ We cannot detect any appreciable structural change for the former alloy, while the latter alloy shows a change to an orthorhombic Cu_8Hf_3 phase with $a_0 = 0.781$ nm, $b_0 = 0.810$ nm and $c_0 = 0.995$ nm. Figure 13 shows bright-field TEM images and selected-area electron diffraction patterns of the annealed alloys. The Cu-Zr-Ti alloy consists of two kinds of cubic phases with lattice parameters of 0.35 nm and 0.53 nm. Considering that the cubic phase with $a_0 = 0.53$ nm exists in the as-spun state, the first-stage exothermic peak is concluded to result from the precipitation of the cubic-CuZr phase with $a_0 = 0.35$ nm. The newly precipitated cubic-CuZr phase has a particle size of about 10–20 nm and disperses homogeneously in coexistence with the original cubic phase. However, we cannot detect distinct grain growth of the original cubic phase in the bright-field TEM image. In

Fig. 12 X-ray diffraction patterns of the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ glassy alloys annealed at the temperatures just above the first exothermic peak.

Fig. 13 Bright-field TEM images and nanobeam diffraction patterns of the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ (a,b,c) and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ (d,e) glassy alloys annealed at the temperatures just above the first exothermic peak.

contrast, the Cu-Hf-Ti phase is occupied by the Cu_8Hf_3 phase over the whole area and its grain size is about 20–30 nm, which is much larger than that of the cubic phase. This result indicates clearly that the first exothermic peak of the Cu-Hf-

Ti alloy is due to the precipitation of Cu_8Hf_3 phase.

We further examined the kinetic behavior of the precipitates by JMA plot analysis of the first exothermic peak corresponding to the precipitation of the cubic-CuZr and Cu_8Hf_3 phases.²³⁾ A good linear relation was obtained in the JMA plots and the Avrami exponent (n -value) was approximated as 2.5 for the precipitation of the cubic CuZr phase and 3.5 for the Cu_8Hf_3 phase. These n -values indicate that the precipitation occurs through the three-dimensional diffusion controlled growth of nuclei at a constant nucleation rate for the cubic CuZr phase and through the interface diffusion controlled growth with decreasing nucleation rate for the Cu_8Hf_3 phase. Thus, the kinetic behavior is significantly different between the two Cu-based alloys. The Arrhenius analyses of incubation period, τ as a function of isothermal temperature, T , were also made for the primary cubic CuZr and Cu_8Hf_3 phases.²³⁾ Good linear relations were recognized and the activation energy for the nucleation of the primary phase is evaluated to be 383 kJ/mol for the Cu-Zr-Ti alloy and 443 kJ/mol for the Cu-Hf-Ti alloy. The much larger activation energy for the Cu-Hf-Ti alloy indicates that the precipitation of the Cu_8Hf_3 phase is much more difficult as compared with the bcc CuZr phase, this being consistent with the difference in the precipitation modes. In addition, one can notice that the much larger supercooled liquid region for the Cu-Hf-Ti alloy originates from the difficulty of the precipitation of the primary Cu_8Hf_3 phase, as is evidenced from the different precipitation mode and the larger activation energy.

As shown in the previous section, the nanobeam EDX data indicate that the nanoscale bcc phase in the as-spun $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloys has Cu-rich alloy compositions. Based on the experimental data, we have tried to form a glassy single phase through further optimization of alloy composition and confirmed that a decrease in Cu content as well as an increase in Hf content causes the formation of a glassy single phase.

7. Cu-Zr-Al and Cu-Hf-Al Based Bulk Glassy Alloys

It was shown that nanocrystal-dispersed bulk glassy alloys were formed in Cu-Zr-Ti and Cu-Hf-Ti alloy systems by the copper mold casting process. These ternary Cu-based bulk glassy alloys do not completely satisfy the following three component rules^{1,2,4)} for stabilization of metallic supercooled liquid and formation of bulk glassy alloys, *i.e.*, (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches above 12% among main constituent elements, and (3) negative heats of mixing among main elements. The deviation from the three component rules is thought to result in the formation of nanoscale crystal-dispersed glassy alloys because of the increase in the stability of the supercooled liquid against crystallization. When the alloy component of these Cu-based alloys is modified so as to satisfy the three component rules, it is strongly expected that the resulting Cu-based alloys will have an enhanced glass-forming ability through an increase in the stability of the supercooled liquid, *i.e.*, through the extension of the supercooled liquid region prior to crystallization. We examined the thermal stability of Cu-Zr-Al and Cu-Hf-Al ternary alloys in which the three component rules are satisfied.

Fig. 14 DSC curves of melt-spun $\text{Cu}_{60-x}\text{Zr}_{40}\text{Al}_x$ ($x = 0$ to 10 at%) glassy alloys.

Figure 14 shows DSC curves of the as-spun $\text{Cu}_{60-x}\text{Zr}_{40}\text{Al}_x$ glassy alloys. The alloys containing 2.5–7.5%Al exhibit a large supercooled liquid region prior to crystallization. A distinct composition dependence of $\Delta T_x (= T_x - T_g)$ for the Cu-Zr-Al ternary glassy alloys is recognized and the largest ΔT_x is 74 K for $\text{Cu}_{55}\text{Zr}_{40}\text{Al}_5$ and $\text{Cu}_{50}\text{Zr}_{42.5}\text{Al}_{7.5}$ alloys. Any deviation from these alloy compositions causes a gradual decrease in ΔT_x . However, it can be seen that large ΔT_x values above 70 K are obtained over a rather wide composition range of 37.5–47.5%Zr and 2.5–7.5%Al. High reduced glass transition temperatures above 0.60 are also obtained over a wide Al content range from 2–6%Al in the alloy series of $\text{Cu}_{60-x}\text{Zr}_{40}\text{Al}_x$ and the highest T_g/T_l is 0.62 for $\text{Cu}_{55}\text{Zr}_{40}\text{Al}_5$. By choosing the Cu-Zr-Al alloys with high T_g/T_l above 0.60, bulk glassy alloy rods with diameters up to at least 3 mm were formed by the copper mold casting process.²⁴⁾ Table 2 summarizes thermal stability and mechanical properties of the Cu-Zr-Al bulk glassy alloys. These Cu-based alloys possess high compressive fracture strength of 2100–2200 MPa with distinct plastic elongation of 0.002–0.004. The fracture of the Cu-based bulk glassy alloys

Fig. 15 Composition dependence of the supercooled liquid region, $\Delta T_x (= T_x - T_g)$ for Cu-Hf-Al ternary glassy alloys.

occurred along a main shear band inclined by 43 degrees to the direction of applied stress, and a typical elongated vein pattern was observed in the fracture surface.

Similar thermal stability and mechanical properties were also obtained for Cu-Hf-Al ternary glassy alloys. Figure 15 shows the composition dependence of ΔT_x for Cu-Hf-Al ternary glassy alloys.²⁵⁾ The large ΔT_x values above 80 K are obtained over a wide composition range of 37.5–50%Hf and 2.5–5%Al and the highest ΔT_x value is 91 K for $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$. Thus, the ΔT_x is strongly dependent on Al content. Table 2 also shows thermal stability and mechanical properties of the Cu-Hf-Al bulk glassy alloys.²⁵⁾ These Cu-Hf-Al bulk glassy alloys exhibit very high compressive fracture strength of 2260–2370 MPa with plastic strain of 0.002–0.006, in addition to high T_g/T_l of 0.62–0.63.

We further examined the additional effect of transition metals (TM=Pt, Au, Pd or Ag) on the thermal stability of supercooled liquid for $\text{Cu}_{50}\text{Zr}_{40}\text{Al}_5\text{TM}_5$ glassy alloys. The addition of Au or Pd increased ΔT_x and the largest ΔT_x was 85 K for the Pd-containing alloy. The extension of the supercooled liquid region results from a more significant increase in T_x in comparison with $\text{Cu}_{55}\text{Zr}_{40}\text{Al}_5$ alloy. A quite remarkable effect on the ΔT_x value was seen with the addition of TM elements to make $\text{Cu}_{45}\text{Hf}_{45}\text{Al}_5\text{TM}_5$ glassy alloys, as shown in Fig. 16.²⁶⁾ All these glassy alloys have large ΔT_x values above 93 K and the largest value is 110 K for the Ag-containing alloy. The increase in the ΔT_x value for the Cu-Hf-Al-Ag alloy is due to the combination of the decrease in T_g and the increase in T_x in comparison with $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$ alloy. Thus, the additional effect of Pd and Ag leading to the increase of ΔT_x is presumably due to an increase in the difficulty of atomic rearrangements on a long-

Table 2 Thermal stability and mechanical properties of Cu-Zr-Al and Cu-Hf-Al bulk glassy alloys.

Composition (at%)	T_g (K)	ΔT_x (K)	T_g/T_l	$\sigma_{c,f}$ (MP)	E (GPa)	$\varepsilon_{c,p}$ (%)	H_v
$\text{Cu}_{55}\text{Zr}_{40}\text{Al}_5$	723	74	0.62	2210	115	0.2	581
$\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Al}_5$	709	71	0.61	2115	111	0.4	573
$\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$	701	72	0.61	1885	102	0.0	546
$\text{Cu}_{50}\text{Hf}_{42.5}\text{Al}_{7.5}$	781	55	0.63	2372	128	0.5	673
$\text{Cu}_{52.5}\text{Hf}_{40}\text{Al}_{7.5}$	779	54	0.63	2344	125	0.6	661
$\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$	763	91	0.62	2262	121	0.2	627

Fig. 16 DSC curves of melt-spun $\text{Cu}_{45}\text{Hf}_{45}\text{Al}_5\text{TM}_5$ (TM=Ag, Pt, Pd or Au) glassy alloys.

Fig. 17 Changes in T_g , T_x and ΔT_x as a function of Ag content for melt-spun $\text{Cu}_{50-x}\text{Hf}_{45}\text{Al}_5\text{Ag}_x$ ($x = 0$ to 10 at%) glassy alloys.

range scale (necessary for the progress of crystallization from supercooled liquid with homogeneously mixed atomic configurations), in addition to an increase in the degree of satisfaction of the three component rules for stabilization of supercooled liquid. Figure 17 shows the changes in T_g , T_x and ΔT_x with Ag content for the $\text{Cu}_{50-x}\text{Hf}_{45}\text{Al}_5\text{Ag}_x$ glassy alloys.^{26,27)} A large ΔT_x above 100 K is obtained in the Ag content range of 5–7.5 at%. In view of previous reports that metallic glassy alloys with large ΔT_x above 100 K are limited to the Zr-Al-Ni-Cu alloy system, the discovery of the new Cu-Hf-Al-Ag and Cu-Hf-Al-Pd glassy alloys is important for the future development of bulk glassy alloys from scientific and engineering points of view.

8. Summary

Glassy phase alloys were formed in $\text{Cu}_{60}\text{Zr}_{40}$, $\text{Cu}_{45}\text{Zr}_{55}$, $\text{Cu}_{55}\text{Hf}_{45}$ and $\text{Cu}_{60}\text{Hf}_{40}$ alloy rods with diameters up to 1.5 mm. The replacement of Zr or Hf by 10 at%Ti causes the formation of bulk glassy alloys containing nanoscale metastable cubic phase particles with a size of about 3–5 nm in cast alloy rods with diameters up to 4 mm. The cubic phase has a lattice parameter of 0.45 nm for the former alloy and 0.51 nm for the latter. The critical diameter for the formation of such a nanostructure was 4 mm for both the alloys. The E , yield strength, $\sigma_{t,f}$, $\sigma_{c,f}$ and $\varepsilon_{c,p}$ are 114 GPa, 1785 MPa, 2000 MPa, 2150 MPa and 0.012, respectively, for the Cu-Zr-Ti bulk alloy and 124 GPa, 2040 MPa, 2130 MPa, 2160 MPa and 0.017, for the Cu-Hf-Ti alloy. The addition of Nb caused an increase in corrosion resistance in various chemical aqueous solutions through the enrichment of elemental Zr, Ti and Nb in the surface film. The ΔT_x is 37 K for the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ alloy and 67 K for the $\text{Cu}_{60}\text{Hf}_{30}\text{Ti}_{10}$ alloy. The primary crystallization of the two nanocrystal-dispersed glassy alloys occurred by the precipitation of a cubic CuZr phase with a lattice parameter of 0.35 nm and an orthorhombic Cu_8Hf_3 phase, respectively. The grain size of their precipitates was 10–20 nm for the CuZr phase and 20–30 nm for the Cu_8Hf_3 phase. The CuZr phase precipitates through the three-dimensional diffusion-controlled growth of nuclei at a constant nucleation rate, while the Cu_8Hf_3 phase has the precipitation mode of interfacial diffusion-controlled growth of nuclei with decreasing nucleation rate. The difference in the precipitation modes is the origin of the difference in the stability of the supercooled liquid. The optimization of alloy components in Cu-based alloys so as to satisfy the three component rules caused the formation of a glassy single phase in Cu-Zr-Al and Cu-Hf-Al ternary systems. Their glassy single phase alloys also exhibit high $\sigma_{c,f}$ of 2100–2370 MPa with $\varepsilon_{c,p}$ up to 0.006. Furthermore, the addition of a small amount of Ag or Pd increases ΔT_x to over 100 K, and the highest ΔT_x value reaches as much as 110 K. These new Cu-based bulk glassy alloys with high glass-forming ability, large ΔT_x of over 100 K and good mechanical properties are promising for the future development of bulk glassy alloys as a new type of structural material.

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