Formation, Thermal Stability and Mechanical Properties of Cu–Zr–Al Bulk Glassy Alloys

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New Cu-based bulk glassy alloys with large supercooled liquid region and high mechanical strength were found to be formed in Cu–Zr–Al ternary system. The large supercooled liquid region exceeding 70 K was obtained in the composition range of 40 at%Zr at 2.5 at%Al, 37.5%Zr to 47.5%Zr at 5%Al and 42.5%Zr at 7.5%Al. The largest \(\Delta T_g\) was 74 K for Cu\(_{55}\)Zr\(_{40}\)Al\(_5\) and Cu\(_{50}\)Zr\(_{42.5}\)Al\(_{7.5}\) alloys and the highest \(T_g/T_l\) was 0.62 for the former alloy. The alloys with large \(\Delta T_g\) values above 70 K were formed into a bulk glassy rod form with diameters up to 3 mm by copper mold casting and the glassy alloy rods exhibit high compressive strength of 1885 to 2210 MPa and Young’s modulus of 102 to 115 GPa combined with elastic elongation of 1.60 to 1.95% and plastic elongation of 0 to 0.4%. The addition of 2.5 to 7.5%Al to Cu–Zr alloys was very effective for the increase in glass-forming ability as well as the stabilization of supercooled liquid. The effectiveness can be interpreted on the basis of the concept of the formation of the unique glassy structure in special multi-component alloys with the three empirical component rules.

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1. Introduction

Recent years, much attention has been paid to the formation and various properties of bulk glassy alloys in conjunction with high stability of supercooled liquid against crystallization. It is well known that the recent attention is attributed to a series of findings of a number of bulk glassy alloys with a large supercooled liquid region in Mg-\(^{1}\) lanthanide (Ln)-\(^{2}\) and Zr-\(^{3}\) based alloy systems for several years between 1988 and 1990. For the last one decade, glassy alloy systems have been remarkably extended to Ti-\(^{4}\) other Zr-based,\(^{5,6}\) Hf-\(^{7}\) Fe-\(^{8,9}\) Co-\(^{10}\) Pd–Cu-\(^{11}\) Cu-\(^{12}\) Ni-\(^{13,15}\) and Ca-\(^{16}\) based alloy systems and the maximum sample diameter is about 80 mm\(^{17}\) for Pd–Cu–Ni–P system, 30 mm\(^{18}\) for Zr-based system, 12 mm\(^{19}\) for Mg-based system and 5 to 8 mm for Ti-\(^{20}\) Fe-\(^{21}\) Cu-\(^{22}\) and Ca-\(^{16}\) based systems.

When we pay attention to high-strength bulk glassy alloys with tensile strength of over 2000 MPa, a number of previous data inform us the limitation of alloy systems to Cu- and Ni-based alloys. It has been reported that the tensile strength is in the range of 2000 to 2800 MPa for the former alloys\(^ {12,22,23}\) and 2600 to 3200 MPa for the latter alloys.\(^ {25}\) It is noticed that these tensile strength values are much higher than those (1500 to 1800 MPa)\(^ {22,25}\) for various Zr-based glassy alloys. As described above, the maximum sample diameter for bulk glassy alloys is above 5 mm for Cu-based alloys and 3 mm for Ni-based alloys.\(^ {22,24}\) It can be thus interpreted that the Cu-based bulk glassy alloys have simultaneously high tensile strength and high glass-forming ability. As main alloy systems of Cu-based bulk glassy alloys which can be defined by Cu contents exceeding 50%, one can list up Cu–Zr–Ti,\(^ {12}\) Cu–Hf–Ti,\(^ {29}\) Cu–Zr–Hf–Ti,\(^ {30}\) Cu–Zr–Ti–Y\(^ {22}\) and Cu–Zr–Ti–Be\(^ {23}\) etc. It is important to search for a new Cu-based ternary alloy system in which bulk glassy alloys with diameters above several millimeters are formed by a copper mold casting method. We have already pointed out that the above-described Cu-based bulk glassy alloys are only exceptional examples which do not satisfy the three empirical rules for formation of bulk glassy alloys and stabilization of supercooled liquid.\(^ {12}\) It is therefore expected that the modification of the alloy components to an appropriate alloy system with the three component rules causes a significant improvement of glass-forming ability and thermal stability of supercooled liquid. This paper intends to present the additional effect of Al, which satisfies the three component rules against Cu and Zr elements, on the formation, thermal stability and mechanical properties of Cu–Zr–Al bulk glassy alloys.

2. Experimental Procedure

Ternary Cu-based alloy ingots with composition of Cu\(_{100−x}\)Zr\(_x\)Al\(_1\) were prepared by arc melting the mixtures of pure Cu, Zr and Al metals in an argon atmosphere. The alloy compositions represent the nominal atomic percentages. Cylindrical rod alloys of about 60 mm in length and 1.5 to 4 mm in diameter were produced by a copper mold casting method. Ribbon samples with a cross section of 0.02 \(\times\) 1.2 mm\(^2\) were also produced by the melt-spinning method. The glassy structure was examined by X-ray diffraction and the absence of micrometer 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 heating rate of 0.67 K/s. The liquidus temperature (\(T_l\)) was examined by 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 2 mm and a length of 4 mm and the strain rate was 5.0 \(\times\) 10\(^{-4}\) s\(^{-1}\). Fracture surface was examined by scanning...
electron microscopy (SEM).

3. Results

3.1 Thermal stability of melt-spun Cu–Zr–Al glassy alloys

We confirmed that a glassy phase was formed in the Cu$_{60-x}$Zr$_{40}$Al$_x$ alloys containing Al contents up to 15% by melt spinning. Figure 1 shows the DSC curves of the Cu$_{60-x}$Zr$_{40}$Al$_x$ ($x = 0$ to 10 at%) glassy alloys. All the alloys exhibit a distinct glass transition, followed by a supercooled liquid region and then exothermic reactions due to crystallization. Based on the DSC curves, the glass transition temperature ($T_g$), crystallization temperature ($T_x$) and supercooled liquid region defined by the difference between $T_g$ and $T_x$, $\Delta T_x (= T_x - T_g)$ are plotted as a function of Al content in Fig. 2. The $T_g$ increases monotonously from 717 to 740 K with increasing Al content to 10%, while the $T_x$ shows a maximum of about 801 K in the Al content range of 5 to 7.5%, leading to a maximum $\Delta T_x$ value of 74 K at 5%Al. It is thus concluded that the addition of 5%Al to Cu–Zr binary glassy alloys is very effective for an increase in $\Delta T_x$, i.e., stabilization of supercooled liquid.

With the aim of evaluating the glass-forming ability of the Cu–Zr–Al alloy composition, we determined the reduced glass transition temperature ($T_g/\alpha$), crystallization temperature ($T_x/\alpha$) and supercooled liquid region for the Cu–Zr–Al glassy alloys. As shown for the DTA curves of the Cu$_{60-x}$Zr$_{40}$Al$_x$ alloys in Fig. 5, the glass transition phenomenon in conjunction with a supercooled liquid region can be observed in a wide Zr content range of 35 to 50 at%. Figure 5 summarizes the $T_g$, $T_x$ and $\Delta T_x$ values as a function of Zr content for the Cu$_{60-x}$Zr$_{40}$Al$_x$ glassy alloys. The $T_g$ decreases monotonously from 762 to 688 K with increasing Zr content to 50 at%, while the $T_x$ shows a maximum of about 810 K at 37.5%Zr and then decreases monotonously with increasing Zr content. The resulting $\Delta T_x$ value shows a maximum value of about 74 K in a wide Zr content range of 37.5 to 47.5%, as shown in Fig. 6. We also measured the $T_1$ of the Cu$_{95-x}$Zr$_x$Al$_5$ glassy alloys. As shown for the DTA curves in Fig. 7, $T_1$ decreases significantly from 1320 to 1166 K with increasing Zr content from 30 to 40 at% and remains constant in a wide Zr content range from 40 to 45 at%. Based on the composition dependence of $T_g$ and $T_x$, the highest $T_g/T_x$ is evaluated to be 0.62 for Cu$_{55}$Zr$_{40}$Al$_5$ and decreases with deviating from the alloy composition. Figure 8 shows the composition dependence of $\Delta T_x$ for the Cu–Zr–Al glassy alloys. The large $\Delta T_x$ values above 70 K are obtained in the wide composition range of 37.5 to 47.5%Zr and 2.5 to 7.5%Al and the largest $\Delta T_x$ is 74 K for Cu$_{55}$Zr$_{40}$Al$_5$ and Cu$_{98}$Zr$_{12.5}$Al$_{7.5}$. Since the

Fig. 1 DSC curves of melt-spun Cu$_{60-x}$Zr$_{40}$Al$_x$ ($x = 0$ to 10 at%) glassy alloys.

Fig. 2 Changes in the glass transition temperature ($T_g$), crystallization temperature ($T_x$) and supercooled liquid region ($\Delta T_x$) as a function of Al content for melt-spun Cu$_{60-x}$Zr$_{40}$Al$_x$ glassy alloys.
Fig. 3 DTA curves of melt-spun Cu_{60-x}Zr_{40}Al_{x} (x = 0 to 10 at%) glassy alloys.

Fig. 4 Changes in the liquidus temperature ($T_l$) and reduced glass transition temperature ($T_g/T_l$) as a function of Al content for melt-spun Cu_{60-x}Zr_{40}Al_{x} glassy alloys.

**alloy exhibiting the largest $\Delta T_x$ and the highest $T_g/T_l$ was Cu_{55}Zr_{40}Al_{5}, it may be concluded that the alloy has the highest glass-forming ability in the Cu–Zr–Al ternary system.**

Fig. 5 DSC curves of melt-spun Cu_{95-x}Zr_{x}Al_{5} glassy alloys.

Fig. 6 Changes in the $T_g$, $T_x$, and $\Delta T_x$ as a function of Zr content for melt-spun Cu_{95-x}Zr_{x}Al_{5} glassy alloys.

**3.2 Formation and properties of bulk glassy Cu–Zr–Al alloy rods**

Figure 9 shows the outer surface appearance of a Cu_{55}Zr_{40}Al_{5} alloy rod with a diameter of 3 mm produced by the copper mold casting method. The cast alloy rod has a smooth outer surface and no concave due to the precipitation of a crystalline phase is seen. We confirmed the absence of any crystalline phase on a micrometer scale over the whole cross section by optical microscopy. Figure 10
shows the X-ray diffraction patterns of the cast bulk glassy Cu_{95-x}Zr_{x}Al_{5} (x = 40, 42.5 and 45 at%) alloys with different diameters of 2 and 3 mm. All the diffraction patterns show only broad peaks, indicating the formation of a glassy phase. Table 1 summarizes mechanical properties and thermal stability of the Cu_{95-x}Zr_{x}Al_{5} (x = 40, 42.5 and 45 at%) alloy rods. The compressive fracture strength, Young’s modulus and Vickers hardness show a distinct composition dependence, i.e., a gradual decrease in these strength values with increasing Zr content, in agreement with the compositional dependence of $T_g$. It is noticed that the Cu_{55}Zr_{40}Al_{5} bulk glassy alloy exhibits simultaneously high glass-forming ability, large supercooled liquid region of 74 K, high $T_g$ of 723 K, high compressive fracture strength of 2210 MPa, high Young’s modulus of 115 GPa, distinct plastic elongation of 0.2% and high Vickers hardness of 581. We also confirmed that the fracture takes place along the maximum shear stress plane which is inclined by about 45 degrees to the direction of applied load and the fracture surface consists mainly of a well-developed vein pattern. It is thus concluded that the addition of only 5% Al to Cu–Zr alloys is effective for an increase in glass-forming ability, thermal stability and mechanical properties.

4. Discussion

We discuss the reason for the significant effect of Al addition to the improvements of the glass-forming ability, thermal stability and mechanical properties of the Cu–Zr–Al glassy alloys. It is well known that no bulk glassy alloy is formed in Cu–Zr binary alloys by the copper mold casting method. The addition of 5% Al has enabled us to form bulk glassy alloy rods with diameters up to 3 mm. It has generally been recognized that the bulk glassy alloys through the stabiliza-
tion of supercooled liquid can be obtained in special multi-component alloy systems which satisfy the following three empirical component rules, \(^{25,26}\) i.e., (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches above 12% among the main three elements, and (3) suitable negative heats of mixing among the main elements. Considering that the atomic size ratio is 1.25 for Zr/Cu and 1.12 for Al/Cu \(^{31}\) and the heat of mixing is \(-23\) kJ/mol for Cu–Zr pair, \(-44\) kJ/mol for Zr–Al pair and \(-1\) kJ/mol for Cu–Al pair, \(^{32}\) the above-described three component rules are satisfied by the addition of Al to Cu–Zr alloys. It has previously been reported that the glassy alloys with the three component rules can have a unique glassy structure with highly dense random packing, new local atomic configuration and long-range homogeneity with attractive interaction. \(^{25,26,28}\) In the glassy structure, the atomic diffusivity is reduced, leading to the suppression of nucleation and growth reactions of a crystalline phase from liquid. In addition, it is interpreted that the increase in the mechanical properties is due to the formation of the unique glassy structure accompanying the increase in the number of attractive bonding of Zr–Al and Cu–Al pairs with large negative values.

5. Summary

We examined the effect of Al addition on the glass-forming ability, thermal stability and mechanical properties of Cu–Zr glassy alloys, with the aim of synthesizing a bulk glassy alloy with high strength in Cu-based alloy system. The results obtained are summarized as follows.

1. As the Al content increases to 10 at\%, \(T_g\) increases monotonously from 717 K at 0%Zr to 741 K at 10%Al, while the \(T_x\) shows a maximum of about 797 K at 5%Zr, leading to a maximum \(\Delta T_g\) of 74 K at 5%Al. The \(T_l\) also shows a minimum of 1166 K at 5%Al, resulting in a maximum \(T_g/T_l\) of 0.62 at 5%Al.

2. The \(T_g\) of the Cu\(_{93−x}\)Zr\(_x\)Al\(_5\) alloys decreases monotonously with increasing Zr content, \(i.e.,\) from 770 K at 32.5%Zr to 688 K at 50%Zr, while \(T_x\) shows a maximum of 810 K at 37.5%Al and decreases with deviating from the Zr content. As a result, \(\Delta T_g\) shows high values of over 70 K in the wide Zr content range of 37.5 to 47.5%Al. \(T_l\) also shows a minimum of about 1165 K at 40 and 42.5%Zr, leading to a maximum \(T_g/T_l\) at 40%Zr.

3. Bulk glassy alloy rods with diameters up to 3 mm were formed for Cu\(_{95−x}\)Zr\(_x\)Al\(_5\) (\(x = 40, 42.5\) and 45%) alloys by copper mold casting. The 40%Zr glassy alloy rod exhibits high compressive fracture strength of 2210 MPa and Young’s modulus of 115 GPa in conjunction with elastic elongation of 1.80% and plastic elongation of 0.2%.

4. The effectiveness of Al addition on the increase in the glass-forming ability, thermal stability and mechanical strength of the Cu–Zr alloys is interpreted in the framework of the formation of the unique glassy structure in the special multi-component alloys with the three empirical component rules.

REFERENCES