Thermal Stability and Mechanical Properties of Cu-Based Bulk Glassy Alloys in $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ System

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The thermal stability, crystallization and mechanical properties of the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) bulk glassy alloys have been investigated. The glass transition temperature (T_g), crystallization temperature (T_x), liquidus temperature (T_l) and the supercooled liquid region $\Delta T_x (= T_x - T_g)$ increase with increasing Hf content. The reduced glass transition temperature (T_g/T_l) is in the range from 0.603 to 0.615. The Vicker's hardness (H_v), Young's modulus (E) and compressive fracture strength ($\sigma_{c,f}$) of the bulk glassy alloys increase linearly with increasing Hf content and reach the maximum values of 627, 121 GPa and 2262 MPa, respectively, for $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$. A different crystallization behavior is observed for $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$ glassy alloys. The final crystallization phases are $\text{Cu}_{10}\text{Zr}_7$ for the former alloy, and $\text{Cu}_{10}\text{Hf}_7$ and CuHf_2 for the latter alloy.

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1. Introduction

It is known that amorphous alloys have characteristic physical and chemical properties such as high strength, high corrosion resistance and good soft magnetic properties, which are significantly different from those of the corresponding crystalline alloys.¹⁾ However, the requirement of rapid solidification has led to strict limitation of their material shape to ribbon, wire and powder and its limitation has restricted further extension of their application fields. Since the findings of glassy-type alloys with a large supercooled liquid region in Mg-Ln-Ni²⁾ and Ln-Al-Ni³⁾ (Ln=lanthanide metals) systems, followed by the successes of producing bulk glassy alloys in the Ln-⁴⁾ and Mg-⁵⁾ based systems by the copper mold casting method, much attention has been paid to the development of new glassy alloys with high glass-forming ability (GFA). As a result, bulk glassy alloy systems have been widely extended to Zr-,^{6,7)} Fe-,⁸⁾ Pd-Cu-,⁹⁾ Co-,¹⁰⁾ Cu-Ti-,¹¹⁾ Ni-Zr-¹²⁾ and Ni-Nb-¹³⁻¹⁵⁾ based alloys. Recently, we have succeeded in developing new Cu-based bulk glassy alloys in Cu-Zr-Ti and Cu-Zr-Al systems.^{16,17)} The Cu-Zr-Al glassy alloys have the following advantage points, *e.g.*, (1) high glass-forming ability leading to the maximum sample diameter of over 3 mm, (2) appearance of a large supercooled liquid region exceeding 70 K leading to warm-working through viscous flow of supercooled liquid,¹⁸⁾ (3) high fracture strength above 1885 MPa, and (4) higher mass density which is effective for enhancement of the penetrative property.¹⁹⁾

Further improvement in characteristics of the Cu-Zr-Al glassy alloys may be possible by addition of alloying elements. Hafnium is chemically analogous to zirconium, though its atomic weight is much larger. Thus, it is speculated that the alloys in which Zr is replaced by Hf would increase density in conjunction with excellent GFA. It has been reported that Zr-based bulk glassy alloys in which Zr is replaced by Hf possess increased mechanical properties.²⁰⁾ However, little is known about the effect of

substitution of Hf for Zr on the thermal stability and mechanical properties of Cu-based Cu-Zr-Al bulk glassy alloys. This paper presents the density, thermal stability and mechanical properties of the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy alloys and to investigate the effectiveness of substitution of Hf for Zr.

2. Experimental Procedure

Multi-component Cu-based Cu-(Hf, Zr)-Al alloy ingots were prepared by arc melting the mixtures of pure Cu, Zr, Hf and Al metals in a Ti-gettered argon atmosphere. The purity of metals was over 99.9 mass%. Alloy ingots were re-melted four times to ensure chemical homogeneity. The mass losses were measured for each ingot after melting and were less than 0.1 mass%. The glassy alloys in a ribbon form with a cross section of $0.02 \times 1.5 \text{ mm}^2$ and in a cylindrical rod form with a diameter of 2 mm were produced by melt spinning and copper mold casting, respectively. The glassy phase was identified by X-ray diffraction and thermal stability 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. The density was measured by Archimedes' principle by weighing ingots in toluene and in air. Vicker's hardness was measured using a microhardness tester under a load of 200 g. Mechanical properties were measured under a compressive load with an Instron testing machine. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height and the strain rate was $5 \times 10^{-4} \text{ s}^{-1}$. The fracture surface was examined by scanning electron microscopy (SEM).

3. Results

The X-ray diffraction patterns showed all that the melt-spun $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) alloy ribbons were composed of a glassy single phase. Figure 1 shows DSC (a)

Fig. 1 Differential scanning calorimetry (a) and differential thermal analytic (b) curves of $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy alloys.

and DTA (b) curves of the melt-spun $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0, 1/4, 1/2, 3/4$ and 1) glassy alloys. All alloys exhibit a distinct glass transition, followed by a supercooled liquid region and then a single exothermic reaction due to crystallization. The solidification of those alloys is completed through a single endothermic reaction leading to a lower liquidus temperature. Based on the DSC and DTA curves, glass transition temperature (T_g) and crystallization temperature (T_x), supercooled liquid region $\Delta T_x (= T_x - T_g)$, liquidus temperature (T_l) and reduced glass transition temperature (T_g/T_l) are plotted as a function of Hf content in Fig. 2. As the Hf content increases, T_x and T_g increase almost linearly and the increase ratio is considerably larger for T_x , resulting in a linear increase from 71 K at $x = 0$ to 91 K at $x = 1$. It is thus concluded that the substitution of Hf for Zr in the Cu-Zr-Al glassy alloys is effective for an increase in ΔT_x . The T_l increases monotonously with increasing Hf content. However, the T_g/T_l gradually increases from 0.603 at $x = 0$ to 0.615 at $x = 3/4$, and then slightly decreases. Here, it is noticed that the large ΔT_x exceeding 70 K and high T_g/T_l above 0.60 are simultaneously obtained in the Hf content range from $x = 0$ to 1, indicating that $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys have high thermal stability of the supercooled liquid and high GFA.²¹⁾

The $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) alloy rods of 2.0 mm in diameter were formed by copper mold casting. Figure 3 shows X-ray diffraction patterns obtained from the transverse cross-sections of the alloy rods. The X-ray diffraction patterns consist only of broad peaks, indicating the formation of a glassy single phase.

We measured the density of the glassy alloy rods. The density increases linearly with increasing Hf content from 7.574 g/cm³ at $x = 0$ to 11.508 g/cm³ at $x = 1$. This is consistent with the density which is predicted on the basis of the known density of Cu-Zr-Al alloys, suggesting that the substitution of Hf for Zr does not significantly alter the

structure of the glassy alloys.

Figure 4 shows the compressive stress-strain curve of the glassy alloys rod of 2.0 mm in diameter. It is seen that the total strain is less than 0.023, with plastic strains of 0 to 0.002, and the fracture strength increases monotonously with increasing Hf content. Figure 5 shows the changes in compressive Vickers hardness (H_V), Young's modulus (E) and fracture strength ($\sigma_{c,f}$) with Hf content for the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy alloys. The H_V , E and $\sigma_{c,f}$ increase almost linearly from 546, 102 GPa and 1885 MPa, respectively, at $x = 0$ to 627, 121 GPa and 2262 MPa, respectively, at $x = 1$. We have also confirmed that the fracture occurs along the maximum shear stress plane which is declined by about 45 degrees to the direction of applied compressive load, and the fracture surface consists mainly of a well-developed vein pattern. It is thus also concluded that the substitution of Hf for Zr for the Cu-(Zr,Hf)-Al glassy alloys is effective for an increase in mechanical properties.

We have examined crystallization behavior of the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys by X-ray diffraction. Figure 6 shows X-ray diffraction patterns of the $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ (a) and $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$ (b) alloys annealed for 600 s at various temperatures just below and above the crystallization exotherm. The different crystallization behavior was observed for the glassy alloys with $x = 0$ and $x = 1$. The final crystallization phases are $\text{Cu}_{10}\text{Zr}_{22}$ for the former alloy, and $\text{Cu}_{10}\text{Hf}_7$ and CuHf_2 for the latter alloy. However, the primary crystalline phase of all $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys is the $\text{Cu}_{10}(\text{Zr,Hf})_7$ phase of an orthorhombic $\text{Ni}_{10}\text{Zr}_7$ type, suggesting that a similar local atomic configurations are formed in the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys. In addition, the precipitation temperature of the $\text{Cu}_{10}(\text{Zr,Hf})_7$ phase increases monotonously with increasing Hf content. From Fig. 6, it is seen that the primary $\text{Cu}_{10}(\text{Zr,Hf})_7$ phase was first identified by XRD for $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ and 1)

Fig. 2 Glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid region ($\Delta T_x = T_x - T_g$), liquidus temperature (T_l) and reduced glass transition temperature (T_g/T_l) as a function of Hf content for $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy alloys.

Fig. 3 X-ray diffraction patterns of cast $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) alloy rods with a diameter of 2.0 mm.

Fig. 4 Compressive stress-elongation curves of $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy rods with a diameter of 2.0 mm.

Fig. 5 H_v , E and σ_{cf} as a function of Hf content for the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy alloy rods.

glassy alloys annealed for 600 s at about 723 and 798 K, respectively.

4. Discussion

The substitution of Hf for Zr in the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys increases significantly the supercooled liquid region ΔT_x . This result has a relation to the thermal stability of their glassy alloys against crystallization. The different crystallization behavior was observed for the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys, the crystallization of the

Fig. 6 X-ray diffraction patterns of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ (a) and $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$ (b) glassy alloys annealed for 600 s at various temperatures.

glassy alloys occurs through a single exothermic peak corresponding to the reactions of glassy $\rightarrow \text{Cu}_{10}\text{Zr}_7$ for $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$, and glassy $\rightarrow \text{Cu}_{10}\text{Hf}_7$ + glassy $\rightarrow \text{Cu}_{10}\text{Hf}_7$ + CuHf_2 for $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$. However, the primary crystalline phase of the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys is the $\text{Cu}_{10}(\text{Zr,Hf})_7$ phase with an orthorhombic $\text{Ni}_{10}\text{Zr}_7$ type structure, and the precipitation temperature of the $\text{Cu}_{10}(\text{Zr,Hf})_7$ phase increases monotonously with increasing Hf content. This indicates that the thermal stability of the glassy alloy against crystallization is enhanced by the increase of Hf content, leading to the increase of ΔT_x .

As shown in Fig. 5, the substitution of Hf for Zr in the Cu-Zr-Al glassy alloys is effective for an increase in the mechanical properties. This seems to originate from the change in the bonding force among the constituent elements of the glassy alloys. It is known that the T_g of the glassy alloys reflects the bonding force among the constituent elements.²³⁾ The T_g of the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ glassy alloys increases linearly with increasing Hf content (Fig. 2), being consistent with the mechanical properties of the glassy alloys.

5. Summary

We examined the stability of supercooled liquid, density and mechanical properties of the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ ($x = 0$ to 1) glassy alloys. The results obtained are summarized as follows.

- (1) In the $\text{Cu}_{50}(\text{Zr}_{1-x}\text{Hf}_x)_{45}\text{Al}_5$ alloy system, the T_g , T_x and T_i increase with increasing Hf content, while the ΔT_x increases linearly from 71 to 91 K with increasing x from 0 to 1. The reduced glass transition temperature (T_g/T_i) is in the range from 0.603 to 0.615.
- (2) The density increases linearly with increasing Hf content, and the increase ratio is 52% when Zr is completely replaced by Hf.
- (3) The H_V , E and $\sigma_{c,f}$ of the bulk glassy alloys increase almost linearly with increasing Hf content. The $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$ bulk glassy alloy exhibits good mechanical properties, i.e., Vicker's hardness of 627, Young's modulus of 121 GPa, compressive fracture strength of 2262 MPa, and plastic

elongation of 0.2%.

- (4) The different intermetallic phases form upon annealing for the $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ and $\text{Cu}_{50}\text{Hf}_{45}\text{Al}_5$ glassy alloys, $\text{Cu}_{10}\text{Zr}_7$ for the former alloy, and $\text{Cu}_{10}\text{Hf}_7$ and CuHf_2 for the latter alloy.

REFERENCES

- 1) F. E. Luborsky (Ed.): *Amorphous Metallic Alloys*, (Butterworths, London, 1983) pp. 1-7.
- 2) A. Inoue, K. Ohtera, K. Kita and T. Masumoto: *Jan. J. Appl. Phys.* **27** (1988) L2248-L2251.
- 3) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans., JIM* **30** (1989) 965-972.
- 4) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans., JIM* **31** (1990) 425-428.
- 5) A. Inoue, A. Kato, T. Zhang, S. G. Kim and T. Masumoto: *Mater. Trans., JIM* **32** (1991) 609-616.
- 6) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans., JIM* **31** (1990) 177-183.
- 7) A. Peker and W. L. Johnson: *Appl. Phys. Lett.* **63** (1993) 2342-2344.
- 8) A. Inoue and S. G. Gook: *Mater. Trans., JIM* **36** (1995) 1180-1183.
- 9) A. Inoue, N. Nishiyama and T. Matsuda: *Mater. Trans., JIM* **37** (1996) 181-184.
- 10) T. Itoi and A. Inoue: *Mater. Trans., JIM* **41** (2000) 1256-1262.
- 11) X. H. Lin and W. L. Johnson: *J. Appl. Phys.* **78** (1995) 5614-5619.
- 12) S. Yi, T. G. Park and D. H. Kim: *J. Mater. Res.* **15** (2000) 2425-2430.
- 13) A. Inoue, W. Zhang and T. Zhang: *Mater. Trans.* **43** (2002) 1952-1956.
- 14) W. Zhang and A. Inoue: *Scr. Mater.* **48** (2003) 641-645.
- 15) H. Choi-Yim, D. Xu and W. L. Johnson: *Appl. Phys. Lett.* **82** (2003) 1030-1032.
- 16) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: *Acta Mater.* **49** (2001) 2645-2652.
- 17) A. Inoue and W. Zhang: *Mater. Trans.* **43** (2002) 2921-2925.
- 18) A. Inoue, Y. Kawamura and Y. Saotome: *Mater. Sci. Forum.* **233-234** (1997) 147-154.
- 19) R. B. Dandliker, R. D. Conner and W. L. Johnson: *J. Mater. Res.* **13** (1998) 2896-2901.
- 20) X. Gu, L. Xing and T. C. Hufnagel: *Mat. Res. Soc. Symp. Proc.* **644** (2001) L12.16.1-L12.16.5.
- 21) A. Inoue: *Acta Mater.* **48** (2000) 279-306.
- 22) P. Villars: *Pearson's Handbook, Crystallographic Data*, (ASM Intern. Materials Park, Ohio, 1997) p. 1514.
- 23) H. S. Chen: *Rep. Prog. Phys.* **43** (1980) 353-432.