Investigation of mechanical properties and devitrification of Cu-based bulk glass formers alloyed with noble metals

Dmitri V. Louzguine*,1, Hidemi Kato, Akihisa Inoue

Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-Ku, Sendai 980-8577, Japan

Received 21 April 2003; revised 9 September 2003; accepted 10 September 2003

Abstract

The mechanical properties, glass-forming ability, supercooled liquid region and devitrification behaviour of the Cu–Zr–Ti–(Pd, Ag, Pt and Au) bulk glass formers were studied by using a mechanical testing machine, X-ray diffraction, transmission electron microscopy, differential scanning calorimetry and isothermal calorimetry. The bulk glassy alloys of diameter 2 mm were formed in the Cu55Zr30Ti10Pd5 and Cu55Zr30Ti10Ag5 alloys while Cu55Zr30Ti10Au5 bulk alloy showed mixed glassy and crystalline structure. No glassy phase was formed in the Cu55Zr30Ti10Pt5 bulk alloy whereas the glassy phase was formed in all of the ribbon samples prepared by rapid solidification. The studied alloys except for the Pt-bearing one have slightly increased compressive fracture or yield strength values compared to ternary Cu 60Zr30Ti10 glassy alloy. At the same time Pd and Au addition significantly expand the supercooled liquid region of Cu–Zr–Ti glassy alloy and increase Young’s modulus. A nanoicosahedral phase is primarily formed in the Cu55Zr30Ti10(Pd,Au)5 glassy alloys in the initial stage of the devitrification process by nucleation and three-dimensional diffusion-controlled growth. Nearly the same quasilattice constant obtained in the Cu55Zr30Ti10(Pd,Au)5 alloys illustrates the same type of the icosahedral phase in these alloys. However, no icosahedral phase was found in the Cu55Zr30Ti10(Ag,Pt)5 alloys.

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Keywords: Bulk glassy alloy; Noble metals; Mechanical properties; Supercooled liquid; Devitrification; Icosahedral phase; Nanoscale phase

1. Introduction

Cu-based bulk glassy alloys were obtained recently in ternary Cu–(Zr or Hf)–Ti systems [1]. The mechanical properties and devitrification behaviour of the binary Cu–Zr [2], ternary Cu60Zr10Ti10 and Cu60Hf25Ti15 [3] as well as quaternary Cu–Zr–Ti–Ni [4] and Cu–Zr–Ti–Co [5] glassy alloys have been studied. In the current paper we investigate influence of additions of noble metals (NM), such as Pd, Ag, Pt and Au, on the mechanical properties, the glass-forming ability, the supercooled liquid region and the devitrification of Cu–Zr–Ti alloy.

An icosahedral phase—a quasicrystal having a long-range quasiperiodic translational order and an icosahedral orientational order, but with no three-dimensional translational periodicity was initially discovered in Al–Mn alloys [6,7]. Later the icosahedral phase was observed in other Al-, Ga-, Ti-, Mg- and Pd-based alloys [8] as well as Cd- [9], Rare Earth- [10], Zn-based [11] alloys. The icosahedral phase has been also produced in NM-free Zr-based glassy alloys as a result of oxygen contamination [12] at more than 1700 mass ppm of O content as well as a result of NM additions at low oxygen content of about 800 mass ppm [13]. Moreover, it was shown that the precipitation of nanoscale icosahedral particles in Zr-based glassy alloys caused appearance of plastic elongation of partially transformed glassy alloys on mechanical testing [13]. In the present paper we also report the formation of the nanoscale icosahedral phase in Cu55Zr30Ti10(Pd,Au)5 alloys.

2. Experimental procedure

Ingots of Cu55Zr30Ti10Pd5, Cu55Zr30Ti10Ag5, Cu55Zr30Ti10Pt5 and Cu55Zr30Ti10Au5 alloys (all alloy compositions are given in nominal at.%) were prepared by arc-melting mixtures of Cu 99.99 mass%, Zr 99.7 mass%, Ti 99.5
mass%, Pd 99.9 mass%, Ag 99.9 mass%, Pt 99.9 mass% and Au 99.9 mass% in purity in an argon atmosphere. From these ingots, ribbon samples of about 20 µm in thickness and 1 mm in width were prepared by rapid solidification of the melt on a single copper roller at a surface velocity of 42 m/s. Bulk cylindrical samples of 2 mm in diameter and 50 mm in length were prepared by copper mold casting. The structure of the samples was examined by X-ray diffractometry with monochromatic Cu Kα radiation. The X-ray diffraction patterns (XRD) of the bulk samples were taken from the cross-section. Compressive tests on the bulk glassy alloy samples were carried out using an Instron-type testing machine at a strain rate of 5 × 10⁻⁴ s⁻¹. A strain-gage indicator was attached to each sample. The cylindrical sample was 2 mm in diameter and 4 mm in length. The phase transformations were studied by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s and differential isothermal calorimetry. During isothermal calorimetry the samples were heated up to the highest possible heating rate of 1.67 K/s. The temperature and enthalpy for the DSC were calibrated within ±0.2 K and ±0.1 J/g using the melting of In as a standard. Transmission electron microscopy (TEM) investigation was carried out using a JEM 2010 (JEOL) microscope operating at 200 kV. The sample for TEM was prepared by the ion polishing technique.

3. Results

As shown in Fig. 1 the structure of the Cu₅₅Zr₃₀Ti₁₀Pd₅ and Cu₅₅Zr₃₀Ti₁₀Ag₅ bulk glassy alloys of diameter 2 mm was found to consist of a glassy phase. The critical diameter for the formation of a single glassy phase in the Cu₅₅Zr₃₀Ti₁₀Pt₅ and Cu₅₅Zr₃₀Ti₁₀Au₅ alloys was below 2 mm. Cu₅₅Zr₃₀Ti₁₀Pt₅ bulk sample had crystalline structure, although a significant volume fraction of a glassy phase was found in the Cu₅₅Zr₃₀Ti₁₀Au₅ alloy. Rapidly solidified ribbon samples with a glassy structure were obtained for all the Cu₅₅Zr₃₀Ti₁₀NM₅ alloys.

Table 1

| NM    | E (GPa) | σ₁ (MPa) | σ₁/2 (MPa) | σ₁/0.5 (MPa) | Plastic deformation (%) | Elastic deformation (%) |
|-------|---------|----------|------------|--------------|------------------------|------------------------|
| −a    | 114     | 2150     | 1785       | 1.1          | 1.7                    |                        |
| Ag    | 112     | 2100     | 2070       | 2030         | 0.35                   | 1.8                    |
| Pd    | 118     | 2270     | 2200       | 2090         | 0.5                    | 1.9                    |
| Au    | 127     | 2230     | 2230       | 2060         | 0.05                   | 1.7                    |

* The data for the base Cu₆₀Zr₃₀Ti₁₀ alloy taken from Ref. [1] are also given for comparison.

The mechanical properties of the studied alloys are summarized in Table 1. The compressive fracture or yield strength values of the Cu₅₅Zr₃₀Ti₁₀Pd₅ and Cu₅₅Zr₃₀Ti₁₀Ag₅ bulk glassy alloys exceed 2000 MPa. The Cu₅₅Zr₃₀Ti₁₀Au₅ bulk alloy with mixed glassy and crystalline structure was also found to exhibit high strength. It’s compressive stress–strain curve is shown in Fig. 2 together with that of the Cu₅₅Zr₃₀Ti₁₀Ag₅ bulk glassy alloy. The Cu₅₅Zr₃₀Ti₁₀Pt₅ bulk sample consisted of the intermetalics and was so brittle to be easily destroyed by hand.

The DSC traces of the ribbon samples demonstrated in Fig. 3 show an increment of C_p at the glass transition temperature (T_g) and the exothermic peaks due to subsequent devitrification starting at T_x (Fig. 3). DSC traces of the Cu₅₅Zr₃₀Ti₁₀Pd₅ and Cu₅₅Zr₃₀Ti₁₀Ag₅ bulk glassy alloys do not differ from those of the ribbon samples.

Although the Cu₅₅Zr₃₀Ti₁₀Au₅ bulk glassy alloy contains some fraction of crystalline phase, it shows high strength of not lower than the Cu₅₅Zr₃₀Ti₁₀(Pd,Ag)₅ glassy alloys. Its DSC curve shown in Fig. 4 is also similar to that of the ribbon sample with glassy structure.

Fig. 1. X-ray diffraction patterns of Cu₅₅Zr₃₀Ti₁₀NM₅ bulk glassy alloys (diameter 2 mm) in as-solidified state. No bulk glassy alloy was formed for Cu₆₀Zr₃₀Ti₁₀Pd₅.

Fig. 2. Compressive stress–strain curve of the Cu₅₅Zr₃₀Ti₁₀(Au,Ag)₅ bulk samples.
The first exothermic peak in the Cu55Zr30Ti10Pd5 alloy is related to the precipitation of primary nanoparticles of the icosahedral phase, as shown in Fig. 5(a). Although, due to the small particle size, the diffraction peaks of the icosahedral phase are broad, the five strongest peaks were identified and indexed (Fig. 5(a)). The indexing of this icosahedral phase has been done according to Elser’s scheme, see Ref. [14]. Calculation gives a quasilattice constant \( a_q = 0.495 \) nm. At the next exothermic peak the icosahedral phase in the Cu55Zr30Ti10Pd5 alloy transforms to the intermediate intermetallic crystalline phase (Fig. 5(b)), which subsequently transforms to an \( \text{oC}68 \) (Pearson Symbol) \((\text{Cu}_2\text{Pd})_{10}(\text{Zr},\text{Ti})_7\) phase (solid solution of Pd and Ti elements in the Cu10Zr7) at higher temperature. This solid solution decomposes at long-term annealing. Similar devitrification behaviour was observed in the ribbon-shaped Cu55Zr30Ti10Au5 alloy.

The structure of the Cu55Zr30Ti10Pd5 sample annealed for 0.6 ks at 785 K is shown in Fig. 6. The average size of the quasicrystalline particles ranged from 3 to 10 nm. The sharp rings in the selected-area electron diffraction pattern correspond to the XRD peaks. The nanobeam diffraction pattern shown in the insert of Fig. 6(a) represents the fivefold symmetry of the icosahedral phase.

The isothermal calorimetry trace of the Cu55Zr30Ti10Pd5 taken at 743 K exhibited an exothermic peak after the incubation period of 1 ks (Fig. 7).

The formation of the icosahedral phase was also observed in the Cu55Zr30Ti10Au5 alloy in the initial stage of devitrification process. The quasilattice constant in the Cu55Zr30Ti10Au5 alloy was found to be \( a_q = 0.496 \) nm.

A metastable crystalline compound was formed during primary devitrification of the Cu55Zr30Ti10Pt5 glassy alloy in a ribbon shape while structural changes in the Cu55Zr30Ti10Ag5 glassy alloy after annealing at the first exothermic peak temperature were not detectable by XRD.

Mechanical tests have been conducted for the Cu55Zr30Ti10Pd5 bulk sample annealed for 0.6 ks at 785 K. Unfortunately, a drastic decrease in the compressive strength (the compressive strength value was only half of that of the as-solidified sample) and totally brittle fracture
The peritectic reaction 'residual glassy phase' to the intermediate crystalline phase through liquid regions.

This allows to estimate volume fraction of the as-solidified phase by 'glassy icosahedral' reaction and its subsequent existence of the crystalline phase.

1. The bulk glassy alloys of diameter 2 mm were formed in the Cu$_{55}$Zr$_{30}$Ti$_{10}$Pd$_{5}$ and Cu$_{55}$Zr$_{30}$Ti$_{10}$Ag$_{5}$ while the Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ bulk alloy has a mixed glassy and crystalline structure. These alloys have slightly increased compressive fracture or yield strength values compared to ternary Cu$_{60}$Zr$_{30}$Ti$_{10}$ glassy alloy.

2. No glassy phase was formed in the Cu$_{55}$Zr$_{30}$Ti$_{10}$Pd$_{5}$ alloy whereas rapidly solidified ribbon samples with a glassy structure were obtained for all the Cu$_{55}$Zr$_{30}$Ti$_{10}$NM$_{5}$ alloys.

3. Pd and Au addition significantly expand the supercooled liquid region of Cu–Zr–Ti glassy alloy and increase the Young’s modulus. The as-solidified crystalline phase in the Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ bulk alloy does not grow or transform below $T_g$ and the sample exhibits clear glass transition (Fig. 4).

An average Goldschmidt atomic diameter for the Pd-bearing alloy $a = 0.280$ nm and quasilattice constant $a_q = 0.495$ nm obtained give the $a_q/(a)$ ratio of 1.77 which indicates that the obtained icosahedral phase is a Bergmann-type quasicrystal [17]. The quasilattice constant in the Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ alloy found to be $a_q = 0.496$ nm illustrating the same type of the icosahedral phase.

4. Discussion

Both the compressive fracture and yield strength values of the Cu$_{55}$Zr$_{30}$Ti$_{10}$Pd$_{5}$ and Cu$_{55}$Zr$_{30}$Ti$_{10}$Ag$_{5}$ bulk glassy alloys are slightly higher than those of the Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy [1] and comparable to those of the Cu–Zr–Ti–Ni [4] and Cu–Zr–Ti–Co alloys [5]. Higher Young’s modulus of the Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ bulk alloy is connected with the existence of the crystalline phase.

The crystallization of the Pt-bearing bulk glassy alloy upon solidification may be connected with a significant rise of the melting temperature by the addition of Pt, the element with the highest melting temperature of 2042 K among NM.

The supercooled liquid region ($\Delta T_s$ defined as a difference between $T_s$ and $T_g$) for Cu$_{55}$Zr$_{30}$Ti$_{10}$Pd$_{5}$ and Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ reached about 50 and 45 K, respectively (Fig. 3). These $\Delta T_s$ values are very close to those of the Cu$_{55}$Zr$_{30}$Ti$_{10}$Ni$_{5}$ [4] and Cu$_{55}$Zr$_{30}$Ti$_{10}$Co$_{5}$ [5] alloys while bulk and ribbon samples of the Cu$_{55}$Zr$_{30}$Ti$_{10}$Ag$_{5}$ and Cu$_{55}$Zr$_{30}$Ti$_{10}$Pt$_{5}$ glassy alloys exhibit narrower supercooled liquid regions.

Enthalpy of the first two overlapped exothermic peaks (the second peak has a small shoulder at higher temperature) responsible for the primary formation of the icosahedral phase by 'glassy → icosahedral' reaction and its subsequent transformation to the intermediate crystalline phase through the peritectic reaction 'residual glassy + icosahedral phase → crystalline intermetallic compound' in the case of ribbon and bulk Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ sample was −57.2 (Fig. 3) and −48.3 J/g (Fig. 4), respectively, whereas the enthalpy of the last heat effect between 900 and 1000 K was almost the same, namely −8.7 and −8.3 J/g, respectively. This allows to estimate volume fraction of the as-solidified crystalline phase in the bulk Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ sample as 19 vol%. One can especially point out that this as-solidified crystalline phase does not grow or transform below $T_g$ and the sample exhibits clear glass transition (Fig. 4).

The isothermal calorimetry trace for the Cu$_{55}$Zr$_{30}$Ti$_{10}$Pd$_{5}$ at 743 K exhibited an exothermic peak after the incubation period of 1 ks which is required for nucleation of the icosahedral phase (Fig. 4). The linearity of the Avrami plot (Fig. 7(b)) indicates that the primary precipitation of the icosahedral phase obeys the following kinetic law [15] for the volume fraction ($x$) transformed as a function of time ($t$):

$$x(t) = 1 - \exp[-Kt^n]$$

(1)

The value of the Avrami exponent obtained, $n = 2.3$ (Fig. 7(b)), is close to 5/2 which corresponds to three-dimensional diffusion-controlled growth of nuclei at a constant nucleation rate [15]. It is known that the icosahedral cluster units in Zr-based alloy can be formed with addition of Pd atoms [16]. Thus, one can suppose that Pd atoms also form icosahedral clusters in Cu–Zr–Ti–Pd alloy.

5. Conclusions

1. Cu$_{55}$Zr$_{30}$Ti$_{10}$ bulk and ribbon samples with almost the same, namely 48.3 J/g and 57.2 J/g, respectively, the enthalpy of the last heat effect between 900 and 1000 K was almost the same, namely −8.7 and −8.3 J/g, respectively. This allows to estimate volume fraction of the as-solidified crystalline phase in the bulk Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ sample as 19 vol%. One can especially point out that this as-solidified crystalline phase does not grow or transform below $T_g$ and the sample exhibits clear glass transition (Fig. 4).

2. No glassy phase was formed in the Cu$_{55}$Zr$_{30}$Ti$_{10}$Pd$_{5}$ bulk alloy whereas rapidly solidified ribbon samples with a glassy structure were obtained for all the Cu$_{55}$Zr$_{30}$Ti$_{10}$NM$_{5}$ alloys.

3. Pd and Au addition significantly expand the supercooled liquid region of Cu–Zr–Ti glassy alloy and increase the Young’s modulus. The as-solidified crystalline phase in the Cu$_{55}$Zr$_{30}$Ti$_{10}$Au$_{5}$ bulk alloy does not grow or transform below $T_g$ and the sample exhibits clear glass transition as well as the ribbon sample with a glassy structure.

4. Nucleation and three-dimensional diffusion-controlled growth of a Bergmann-type nanoicosahedral phase of about 3–10 nm in size from the supercooled liquid region was observed in Cu$_{55}$Zr$_{30}$Ti$_{10}$(Pd, Au)$_5$ in the initial stage of the devitrification process. The icosahedral phase has a metastable nature and transforms to equilibrium crystalline phase(s) through an intermediate...
5 The Cu₅₅Zr₃₀Ti₁₀Pd₅ bulk sample annealed for 0.6 ks at 785 K showed a drastic decrease in the compressive strength and brittle fracture without any detectable plastic elongation.

Acknowledgements

This work was partially supported by a Joint Research Project under The Japan–Korea Basic Science Cooperation Program.

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