Joining Technology for New Metallic Glasses and Inorganic Materials

DEVITRIFICATION BEHAVIOR AND CRYSTAL-GLASSY MIXED-PHASE STRUCTURES OBSERVED IN PARTIALLY CRYSTALLIZED Cu-BASED GLASSY ALLOYS

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ABSTRACT

We studied Cu-Zr-based alloys having exceptionally high glass-forming ability (GFA), and investigated the influence of Ag and Al on the GFA and crystallization behavior. Most of the bulk glassy alloys studied do not contain any crystals in the as-solidified state. The crystallization kinetics of $Cu_{55}Zr_{45}$, $Cu_{50}Zr_{50}$, $Cu_{55-x}Zr_{45}Ag_x$ (x = 0, 10, 20), $Cu_{45}Zr_{45}Al_5Ag_5$, $Cu_{55}Zr_{30}Ti_{10}Ag_5$, $Cu_{55}Hf_{25}Ti_{15}Ag_5$, $Cu_{44}Ag_{15}Zr_{36}Ti_5$ and $Cu_{36}Zr_{48}Al_8Ag_8$ glassy alloys was analyzed. $Cu_{35}Zr_{45}Ag_{20}$ alloy exhibits possible phase separation upon heating within the supercooled liquid region prior to crystallization. The depletion of Ag in the residual glassy phase results in the higher thermal stability of $Cu_{35}Zr_{45}Ag_{10}$ versus $Cu_{35}Zr_{45}Ag_{20}$. $Cu_{50}Zr_{50}$ undergoes primary crystallization, forming a metastable monoclinic CuZr phase, while $Cu_{55}Zr_{45}$, $Cu_{45}Zr_{45}Ag_{10}$, $Cu_{35}Zr_{45}Ag_{20}$ and $Cu_{45}Zr_{45}Al_5Ag_5$ undergo eutectic crystallization, forming mostly stable phases. $Cu_{50}Zr_{50}$, $Cu_{55}Zr_{30}Ti_{10}Ag_5$ and $Cu_{55}Hf_{25}Ti_{15}Ag_5$ undergo nanocrystallization. Although some differences in the crystallization behavior between $Cu_{55-x}Zr_{45}Ag_x$ (x = 0, 10, 20) and $Cu_{45}Zr_{45}Al_5Ag_5$ were found, this may not be the only reason Al and Ag additions improve the GFA of the Cu-Zr alloy. The difficulty in nucleating the tP4 $AgZr^{55}$ phase may be responsible for the high glass-forming ability of the $Cu_{36}Zr_{48}Al_8Ag_8$ and $Cu_{44}Ag_{15}Zr_{36}Ti_5$ alloys.

INTRODUCTION

The structure and properties of bulk glassy alloys have been widely studied since the late 1980's [1,2,3]. Cu-Zr-based alloys exhibit good potential for industrial applications. However, the glass-forming ability (GFA) of Cu-rich alloys has been limited [4]. Several attempts have also been made to increase the GFA of these alloys based on different criteria. These include a reduced glass transition temperature, $T_{rg} = T_g/T_l$ [5], where T_g is the glass-transition temperature and T_l is the liquidus temperature; the width of the supercooled liquid region (ΔT_x) defined as T_x-T_g, where T_x is the crystallization onset temperature, and $\gamma=T_x/(T_g+T_l)$ [6]. Binary Cu-Zr and Cu-Hf bulk glassy alloys were reported to form, though only in narrow composition ranges [7]. It was also reported that some of these binary glasses contained nanocrystals in the as-quenched condition [8]. The addition of a third element like Ti [9] or Al [10], for example, produced dense packing [11], and enhanced the GFA [12] of the binary alloys [13]. Thus, $Cu_{36}Zr_{48}Al_8Ag_8$ could be produced in a fully glassy state with a maximum diameter of 25 mm [14]. The structure and crystallization behavior of some binary Cu-Zr [15], ternary Cu-Zr-Ti [16,17,18,19], and some quaternary Cu-based [20] glassy alloys were studied in detail. The nanocrystal-glassy Cu-Zr [8] and Cu-Zr-Al [21,22] composites showed a large room-temperature compressive plastic deformation of up to 50%. Ag drastically improved the GFA of Cu-Zr-Ti alloys [23] $Cu_{45}Zr_{45}Ag_{10}$ exhibited a relatively high GFA and a high mechanical strength[24].

Following the above findings, the role of Al and Ag to improve the GFA of different Cu-based alloys, their thermal stability, and their crystallization behavior were studied in the present work. Another purpose is to find a possible link between the crystallization behavior and GFA of the alloys.

EXPERIMENTAL PROCEDURE

The ingots of the $Cu_{55}Zr_{45}$, $Cu_{50}Zr_{50}$, $Cu_{55-x}Zr_{45}Ag_x$ (x = 10, 20), $Cu_{45}Zr_{45}Al_5Ag_5$, $Cu_{55}Zr_{30}Ti_{10}Ag_5$, $Cu_{55}Hf_{25}Ti_{15}Ag_5$, $Cu_{44}Ag_{15}Zr_{36}Ti_5$ and $Cu_{36}Zr_{48}Al_8Ag_8$ glassy alloys (compositions are given in nominal atomic percentages) were prepared by arc-melting mixtures of (99.9 wt.% purity) under an argon atmosphere. From these ingots, ribbon samples of about 20 μm thickness and 1 mm width were prepared by melt spinning on to a single copper roller at a roller tangential velocity of about 40 m/s. Bulk rod samples of more than 1 mm diameter were prepared by the copper-mold casting technique. The structure of both the ribbon and rod samples was examined by X-ray diffractometry (XRD) with monochromatic CuK_α radiation. A high-resolution field-emission scanning electron microscope (SEM Hitachi S-4800) equipped with an energy dispersive X-ray spectrometer (EDS) was also used for structural characterization of the polished cross-sections. Phase transformations were studied by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s and differential isothermal calorimetry (DIC). Transmission electron microscopy (TEM) investigations were carried out using a JEOL JEM 2010 microscope operating at 200 kV and equipped with an energy dispersive X-ray spectrometer (EDS) of 0.1 keV resolution. Samples for TEM were prepared first mechanically and subsequently by an ion-polishing technique. In order to avoid structural damage the ion-beam energy was kept below 2 keV. The oxygen content in the studied alloys was kept below 500 ppm (by weight).

RESULTS AND DISCUSSION

Most of the bulk glassy alloys studied do not contain any crystals in the as-solidified state while some samples like $Cu_{44}Ag_{15}Zr_{36}Ti_5$ studied by TEM were found to contain well developed medium-range order zones and even nanoparticles in a bulk form. For example, the structure of the $Cu_{36}Zr_{48}Al_8Ag_8$ metallic bulk glass-forming alloy studied by high-resolution transmission electron microscopy (HRTEM) is shown in Fig. 1. On prolonged observation in the TEM, the glassy phase partially crystallized. Nanocrystals were detected after about 120 s of observation under focused beam which is typical for some Cu-based glassy alloys[25].

Following our Fig. 1 and our recent XRD studies one can suggest that the medium-range order in the studied Cu-Zr-based alloys maintains up to about 2 nm distance [26]. It is also shown that the interatomic distances in the first coordination shell correspond to those of some crystalline compounds used as glassy-phase approximants [27].

The GFA and the crystallization behavior of glassy alloys were analyzed and are summarized in Table I. Natural logarithm of the critical diameter as an indicator of the GFA is plotted as a function of T_{rg} and γ parameter in Fig. 2. Although, some other indicators of the GFA give a better correspondence than T_{rg} [28,29], T_{rg} correlates quite well with the critical diameter of Cu-Zr-based alloys belonging to the similar systems studied in the present work.

Both Ag-bearing and Ag-free alloys exhibit devitrification forming of a supercooled liquid region and subsequent formation of the equilibrium crystalline phases. The addition of Ti causes nanocrystallization of Cu-Zr-Ag as well as Cu-Zr and Cu-Hf alloys (see Fig. 3 illustrating HRTEM image and nanobeam electron diffraction (NBD) pattern) though the XRD pattern of the annealed sample still does not show any sharp peaks (Fig. 4). The $Cu_{50}Zr_{50}$ glassy alloy exhibited a primary crystallization behavior forming a metastable monoclinic mP4 CuZr phase while $Cu_{55}Zr_{45}$, $Cu_{45}Zr_{45}Ag_{10}$, $Cu_{35}Zr_{45}Ag_{20}$, $Cu_{50}Zr_{45}Al_5$ and $Cu_{45}Zr_{45}Al_5Ag_5$ glassy alloys showed rather eutectic crystallization forming mostly equilibrium phases (Fig. 5). For example, the simultaneous formation of oC68 $(Cu,Ag)_{10}Zr_7$ and tP4 (Ag,Cu)Zr solid solution phases in the Cu-Zr-Ag alloys by nucleation and 3-dimensional interface-controlled growth of nuclei indicates rather eutectic crystallization. Although, some difference in the crystallization behavior of $Cu_{55-x}Zr_{45}Ag_x$, $Cu_{50}Zr_{45}Al_5$ and $Cu_{45}Zr_{45}Al_5Ag_5$ glassy alloys was found as shown in Table I it may be not the only reason for

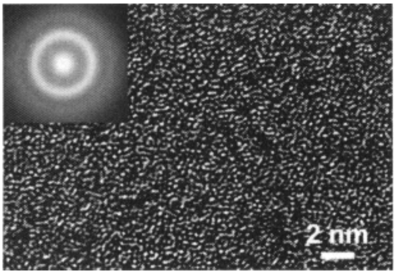

Figure 1. Typical HRTEM image of the $Cu_{36}Zr_{48}Al_8Ag_8$ glassy alloy. The insert is selected-area diffraction pattern.

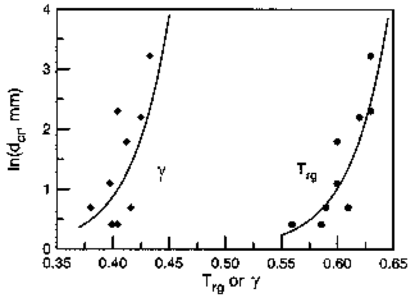

Figure 2. Natural logarithm of the critical diameter as a function of T_{rg} and γ parameter given in Table I.

Table I. GFA, natural logarithm of critical diameter (d_{cr}) and crystallization behavior of the Cu-Zr-based alloys studied. IR-initial crystallization reaction.

Alloy	ln(d_{cr}, mm)	T_g/T_l	γ	IR	Phase composition*
$Cu_{55}Zr_{45}$	0.41	0.59	0.399	Eutectic	oC68 $Cu_{10}Zr_7$+ cP2 CuZr
$Cu_{50}Zr_{50}$	0.69	0.59	0.380	Primary	mP4 CuZr
$Cu_{45}Zr_{45}Ag_{10}$	1.79	0.60	0.412[30]	Eutectic	oC68 $Cu_{10}Zr_7$ and tP4 AgZr
$Cu_{35}Zr_{45}Ag_{20}$	0.41	0.56	0.404	Eutectic	oC68 $Cu_{10}Zr_7$ and tP4 AgZr
$Cu_{55}Zr_{30}Ti_{10}Ag_5$	1.1	0.60	0.397	Primary	nanoscale, unidentified
$Cu_{50}Zr_{45}Al_5$	0.69	0.61[31]	0.416	Eutectic	oC68 $Cu_{10}Zr_7$ + unidentified
$Cu_{45}Zr_{45}Al_5Ag_5$	2.20	0.62[32]	0.425	Eutectic	oC68 $Cu_{10}Zr_7$, cF16 Cu_2AlZr and tP4 AgZr
$Cu_{44}Ag_{15}Zr_{36}Ti_5$	2.30	0.63[25]	0.404	Primary	tP4 AgZr
$Cu_{36}Zr_{48}Al_8Ag_8$	3.22	0.63	0.433	Primary	tP4 AgZr

* a certain solid solubility of other alloying elements is found in some of the binary phases.

the improvement of the GFA of the Cu-Zr alloys by Al and Ag addition.

Contrary to the $Cu_{45}Zr_{45}Al_5Ag_5$ alloy in which a mixture of oC68 $Cu_{10}Zr_7^{ss}$, cF16 Cu_2AlZr and tP4 $AgZr^{ss}$ (ss denotes solid solution) phases was found to form directly by a single-stage eutectic-type reaction and other similar eutectic alloys, the $Cu_{36}Zr_{48}Al_8Ag_8$ alloy exhibited a primary precipitation of tP4 $AgZr^{ss}$ phase upon crystallization on heating. $Cu_{36}Zr_{48}Al_8Ag_8$ and $Cu_{44}Ag_{15}Zr_{36}Ti_5$ alloys have a higher glass-forming ability than the $Cu_{45}Zr_{45}Al_5Ag_5$ alloy but exhibited a primary crystallization. The first DSC exothermic peak in the $Cu_{36}Zr_{48}Al_8Ag_8$ alloy exhibits two shoulders while a single-stage transformation takes place in the $Cu_{45}Zr_{45}Al_5Ag_5$ alloy suggesting that this is close to the eutectic composition. The values of the Avrami exponent close to 4 observed upon the isothermal crystallization of the eutectic alloys supports this conclusion.

$Cu_{35}Zr_{45}Ag_{20}$ alloy exhibited possible phase separation upon heating within the supercooled liquid region prior to crystallization of the liquid. Fig. 6 represents a globular residual amorphous phase surrounded by crystalline (Ag,Cu)Zr and $(Cu,Ag)_{10}Zr_7$ phases. The depletion of the residual glassy phase in Ag as tested by EDX in TEM argues for the higher thermal stability of the $Cu_{35}Zr_{45}Ag_{10}$ glassy phase versus $Cu_{35}Zr_{45}Ag_{20}$.

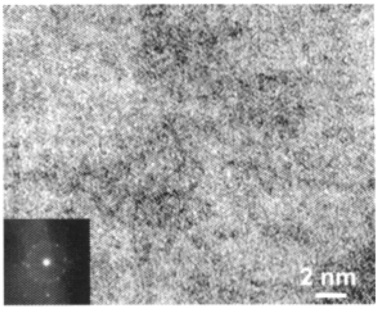

Figure 3. HRTEM image of the $Cu_{55}Hf_{25}Ti_{15}Ag_5$ alloy annealed at 770 K for 300 s. The insert is NBD pattern.

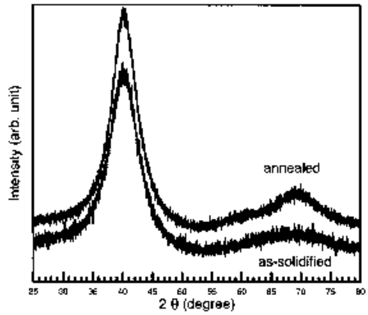

Figure 4. XRD patterns of the $Cu_{55}Hf_{25}Ti_{15}Ag_5$ alloy in as-solidified and annealed at 770 K for 300 s state.

The structure of the nanoscale phases in $Cu_{55}Zr_{30}Ti_{10}Ag_5$ and $Cu_{55}Hf_{25}Ti_{15}Ag_5$ alloys remained unknown owing to their small size. One should also admit a very high density of the precipitates (Fig. 3). Contrary to Cu-Zr-Ti-(Pd,Au) alloys containing noble metals in which formation of the nanoscale icosahedral phase was observed[33] the Ag-containing glassy alloys studied in the present work did not form the icosahedral phase on crystallization.

No significant difference is found in the glass-transition temperature of the melt-spun ribbons and bulk glassy rods of $Cu_{36}Zr_{48}Al_8Ag_8$. On annealing the melt-spun ribbon sample at 744 K for 480 s, primary crystallization led to the formation of tP4 AgZr[55] phase. An unidentified phase was also present. Additionally, the oC68 $Cu_{10}Zr_7$[55] phase formed at higher temperatures. On annealing the ribbon sample at a higher temperature of 900 K for 300 s, crystallization was complete resulting in the formation of the tI6 Zr_2Cu crystalline phase.

In the case of the bulk (10-mm-diameter rod) samples formation of the AgZr[55] phase was also observed in the initial stage of crystallization. The $Cu_{10}Zr_7$ phase also formed in the bulk sample on heat treating at 900 K, and a well-defined fraction of the $CuZr_2$ phase is present after long term annealing. However, even at such a high temperature the structure is not in equilibrium after annealing for 84.6 ks. Only on annealing at 1000 K the ribbon and bulk samples attained the equilibrium structure which indicates a very high stability of the intermediate phases.

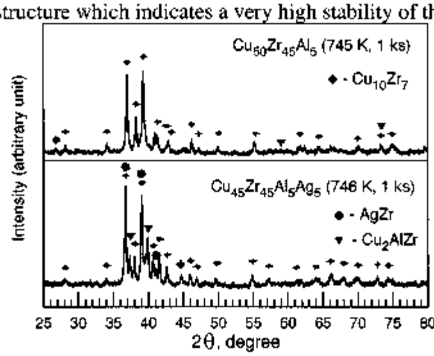

Figure 5. XRD patterns of some alloys in a heat-treated state.

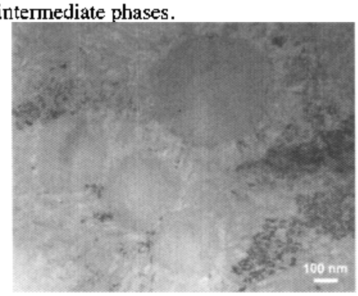

Figure 6. $Cu_{35}Zr_{45}Ag_{20}$ alloy annealed at 722 K for 1 ks, bright-field image, TEM.

Difficulty of nucleation of tP4 AgZr[55] phase may be the reason for the high glass-forming ability of $Cu_{36}Zr_{48}Al_8Ag_8$ and $Cu_{44}Ag_{15}Zr_{36}Ti_5$ alloys. Although this phase has quite a simple structure it contains a large fraction of Ag which is rather a minor alloying element in the alloys, and thus, diffusion redistribution of the alloying elements is required upon its formation, which may slow down the crystallization kinetics.

CONCLUSIONS

The crystallization behavior of $Cu_{55}Zr_{45}$, $Cu_{50}Zr_{50}$, $Cu_{55-x}Zr_{45}Ag_x$ (x = 0, 10, 20), $Cu_{45}Zr_{45}Al_5Ag_5$, $Cu_{55}Zr_{30}Ti_{10}Ag_5$, $Cu_{55}Hf_{25}Ti_{15}Ag_5$, $Cu_{44}Ag_{15}Zr_{36}Ti_5$ and $Cu_{36}Zr_{48}Al_8Ag_8$ glassy alloys was analyzed. $Cu_{35}Zr_{45}Ag_{20}$ alloy exhibited possible phase separation upon heating within the supercooled liquid region prior to crystallization. The depletion of Ag in the residual glassy phase results in the higher thermal stability of the $Cu_{35}Zr_{45}Ag_{10}$ versus $Cu_{35}Zr_{45}Ag_{20}$. $Cu_{55}Zr_{45}$, $Cu_{45}Zr_{45}Ag_{10}$, $Cu_{35}Zr_{45}Ag_{20}$ and $Cu_{45}Zr_{45}Al_5Ag_5$ glassy alloys show a eutectic-type crystallization, forming mostly stable phases. The addition of Ti causes nanocrystallization of Cu-Zr-Ag as well as Cu-Zr and Cu-Hf alloys. Although some difference in the crystallization behavior of $Cu_{55-x}Zr_{45}Ag_x$ (x = 0, 10, 20) and $Cu_{45}Zr_{45}Al_5Ag_5$ glassy alloys was found, this may not be the only reason for the improvement in the GFA of the Cu-Zr alloys with the addition of Al and Ag. The difficulty in nucleating tP4 AgZr[55] may be responsible for the high glass-forming ability of $Cu_{36}Zr_{48}Al_8Ag_8$ and $Cu_{44}Ag_{15}Zr_{36}Ti_5$ alloys.

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