New bulk glassy alloys in Cu-Zr-Ag ternary system prepared by casting and milling

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Abstract. The thermal stability, crystallization behaviour and glass forming ability of Cu-Zr-Ag system have been investigated on the basis of a ternary phase diagram. We altered the concentration of the alloys from the Cu 58Zr42 to the concentration of the deep eutectic point of the Cu-Zr-Ag ternary system and we calculated the glass forming ability parameters. This paper summerises the results of the procedure during which Cu-Zr-Ag amorphous alloys with different Ag content (0-25%) were prepared by casting and ball-milling. Wedge-shaped samples were prepared from the ingots by centrifugal casting into copper mold. The supercooled liquid region (ΔTx) exceeded 75K. Following the characterization of the cast alloys, master alloys of identical composition were milled in a Fritsch Pulverisette 2 ball-mill. The powders, milled for various periods of time were analysed by XRD in order to define the amorphous fraction.

1. Introduction

Vast research has been conducted in order to develop new bulk metallic glasses (BMG) with improved glass-forming ability (GFA) that are also suitable for the development of engineering materials. The Cu-Zr bulk glassy alloy system has been studied to the fullest details [1,2,3]. In order to achieve a copper-based bulk amorphous alloy with larger size it is necessary to add other alloying elements together with the zirconium. The third element such as Ti [4] or Al [5] generally enhances commonly the glass-forming ability. Previous researches have revealed that Ag is an optimal selection for the Cu-Zr system. In the Cu-Zr-Ag system the atomic size ratios are 1,25 for Zr-Cu, 1,10 for Zr-Ag and 1,13 for Ag-Cu. The heat of mixing for Cu-Zr, Zr-Ag and Cu-Ag pairs are -22, -38 and 2kJ/mol respectively [6]. Considering the Zhang Bangwei GFA criterion [7] the Ag element is a favourable alloying element. The Cu–Zr–Ag ternary alloys have a good combination of strength, ductility and thermal stability [6,8]. The individual compositions of the bulk glassy alloys with high GFA are usually close to a deep eutectic composition; for this very reason it is essential to know the phase diagram of the Cu-Zr-Ag system, and particularly the liquidus projection. Up to the present date only a few works have been dedicated to the phase diagram of the Cu-Zr-Ag ternary system. In respect of the ternary eutectic composition there is a divergence of opinions. According to A.A.Kündig et al the composition of a ternary eutectic is Ag19Cu42Zr36 [9]; however in one thermodynamic description given by X.C.He et al [10] the composition of a ternary eutectic is located in the territory with an elevated Ag and Zr content. They fail to give the exact composition of the ternary eutectic and they merely draw the approximate liquidus projection. To the best knowledge of the authors the Ag content
of the samples published up to date does not achieve and exceed the 19%. In 2006 Kündig et al.
published that it is a liquid phase miscibility gap in the Cu-Zr-Ag ternary system [6]. Amorphous powders may be produced by high energy deformation processing via mechanical milling (MM). Depending on the alloy system, the range of compositions that can be mechanically amorphized is similar or wider than those in the melting process. This is an advantage because there is no critical thickness as it is experienced in the melt processing of metallic glass-forming alloys [11].

2. Experimental procedures

Within the Cu-Zr-Ag system the ingots were prepared in a wide range of 37.5-58at% Cu, 35-42at% Zr and 0-22.5at%Ag. The ingots were prepared by arc melting high purity elements of 99.99% purity under argon atmosphere (99.999%) with and without Ti getter. The ingots were re-melted at least four times in order to ensure chemical homogeneity. Wedge-shaped samples were produced from the ingots by centrifugal casting into copper mold under argon atmosphere. The maximum thickness of the wedge-shaped samples is 3mm. Before the mechanical milling the master alloy ingot was ground and fractioned to particle size of < 320 µm. The overall MM process lasted 2 hours and thereafter it was interrupted every 30 minutes. The as-milled powders were extracted in order to examine the progress of the amorphization reaction. The mechanical milling was performed in a high energy planetary Pulverisette2 ball-mill in argon atmosphere using stainless vial and balls with a diameter of about 10 mm. The ball-to-powder ratio was 20:1. The thermal analysis was performed by a Netzsch 204 differential scanning calorimetry (DSC) at heating rates ranging from 5 to 60 °C/min under Ar atmosphere in order to determine the glass transition temperature (Tg) the onset crystallization temperature (Tx) and the peak temperature of the first crystallization (Tp). The liquids temperatures (T) were measured with a differential thermal analyzer (DTA). The individual structure of all samples was confirmed by Phillips PW 1830 X-ray diffractometry (XRD) using Cu Kα radiation (λ=1.5418 nm), and 1830I Amray Scanning Electron Microscope (SEM).

3. Results and discussion

The different thicknesses of the wedge-shaped samples lead to varying cooling rates upon solidification, which results in different microstructures and volume fraction of the crystallizing phase.

Fig. 1,a) shows the SEM images of the etched cross section of the wedge-shaped sample in the case of Cu37,5Zr37,5Ag25 sample. This sample is produced by arc-melting in argon atmosphere purified without using any Ti-getter. Some crystals were observed already near the tip. This phenomenon was experienced in all samples. In the event that the ingots were prepared in argon atmosphere purified with Ti-getter the structure has become fully amorphous near the tip (Fig.1b). If the XRD pattern is measured on the cross section of the samples the results show that the boundary of the fully amorphous structure (Dmax) is between 0.64mm and 0.84mm (Fig.3) however the SEM images of the
cross section demonstrate that there are little crystals present in the territory within the range of \(D_{\text{max}}=107\,\mu\text{m}\) (Fig.2). This phenomenon occurred in all samples. All things considered the maximum section size of BMG \((D_{\text{max}})\) depends on the measurement techniques.

All the alloys exhibit a distinct glass transition, followed by a supercooled liquid region and then exothermic reactions due to crystallization. Fig. 4 demonstrates that the glass forming temperature increases from 427.8°C to 459.8°C together with the increase of the Ag content to 5.8%, thereafter such temperature decreases with a further increase in the Ag-content to 25%. The supercooled liquid region \((\Delta T)\) decreases from 50.7°C to 24.8°C by increasing the Ag content to 20%, thereafter increases to 75°C (measured at 40°C/min) with a further increase in Ag-content to 25% (Fig.5). The less supercooled liquid region is near to the ternary eutectic point Ag_{19}Cu_{45}Zr_{36} \([9]\), and the largest supercooled liquid region approaches to the ternary eutectic point mentioned in the thermodynamic description \([10]\). The supercooled liquid region of samples prepared with Ti getter is approximately higher by about 10°C than the supercooled liquid region of the samples prepared without any Ti getter. Table 1 lists the thermal parameters of the glassy alloys. The apparent activation energy for glass transition and the first crystallization of amorphous alloys were calculated from the DSC measurements by using the Kissinger equation. The most remarkable change is in the apparent activation energy for glass transition; however the value of the statistical correlation parameter has evidenced a modest correlation in our calculations (averagely 0.87). The alloy Cu_{45}Zr_{35}Ag_{20} deviate from the other composition but this is comprehensible, because this alloy is on the border of the miscibility gap at 700K, and the cross-section of the sample shows the typically monotectic structure.
The selected alloys belong to the same liquid area and in them the same phases crystallize during the cooling process, and we calculated the GFA parameters of these alloys. All $\gamma$ values ($\gamma = T_x/(T_g+T_l)$) are higher than 0.4. The $\sigma$ parameters [12] change from 0.23 to 0.25.

Table 1. Thermal Analyses Results of Cu-Zr-Ag alloy series (Heating rate 40K/min)

| Alloy composition | $T_g$, K | $T_x$, K | $T_p$, K | $E_{T_g}$, kJ/mol | $E_{T_x}$, kJ/mol | $E_{T_p}$, kJ/mol | $\gamma$ | $\sigma$ |
|-------------------|----------|----------|----------|-------------------|-------------------|-------------------|--------|--------|
| Cu$_{58}$Zr$_{42}$ | 733      | 781      | 784      | 391               | 374               | 406               |        |        |
| Cu$_{56.3}$Zr$_{40.9}$Ag$_{2.8}$ | 728      | 782      | 784      | 385               | 361               | 444               |        |        |
| Cu$_{53.5}$Zr$_{47.7}$Ag$_{9.8}$ | 733      | 782      | 783      | 385               | 361               | 444               |        |        |
| Cu$_{40.5}$Zr$_{75}$Ag$_{14.8}$ | 721      | 763      | 763      | 373               | 363               | 430               |        |        |
| Cu$_{42.7}$Zr$_{37.3}$Ag$_{15.7}$ | 717      | 752      | 755      | 635               | 423               | 421               | 0.414  | 0.246  |
| Cu$_{39}$Zr$_{43}$Ag$_{20}$ | 720      | 745      | 754      | 635               | 423               | 421               | 0.414  | 0.246  |
| Cu$_{38.2}$Zr$_{43.9}$Ag$_{19}$ | 701      | 751      | 754      | 635               | 423               | 421               | 0.414  | 0.246  |
| Cu$_{40}$Zr$_{39}$Ag$_{19}$ | 689      | 748      | 750      | 635               | 423               | 421               | 0.414  | 0.246  |
| Cu$_{38.7}$Zr$_{43.5}$Ag$_{18.5}$ | 691      | 756      | 760      | 635               | 423               | 421               | 0.414  | 0.246  |
| Cu$_{36}$Zr$_{42}$Ag$_{20}$ | 689      | 754      | 755      | 635               | 423               | 421               | 0.414  | 0.246  |
| Cu$_{40}$Zr$_{39}$Ag$_{18}$ | 706      | 764      | 766      | 635               | 423               | 421               | 0.414  | 0.246  |

Fig. 6 shows the X-ray diffractogram of CuZrAg powders following mechanical milling with a duration of 30, 60, 90, and 120 minutes respectively. After 30 min the alloy shows crystalline phases, which are followed by a mixed state where both crystalline and amorphous phases are present at 60-90 min. Following 120 minutes of mechanical milling the crystalline peaks almost disappear, indicating that the amorphisation of this alloy is nearly complete. This milling time is very short and proves the effectiveness of the mechanical milling of the amorphisable alloys.

4. Summary

Up to present date few works dedicated to the Cu-Zr-Ag ternary system. We have changed the concentration of the alloys from the Cu$_{58}$Zr$_{42}$ to the concentration of the deep eutectic point of Cu-Zr-Ag ternary system. The maximum section size of BMG ($D_{max}$) depends on the measurement technique. Although we have restricted the contamination of samples (oxygen <200ppm) and the largest supercooled liquid region is 75°C we have not succeeded in producing any fully amorphous samples with a thickness exceeding 1mm.

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