[1]The Role of Casting Temperature in Preparation of Bulk Metallic Glasses

Hao Wang

Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

wangh@usq.edu.au

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Abstract. In the past research on bulk metallic glasses (BMGs) has been concentrated on searching for alloy composition to obtain high glass forming ability. Very few studies are on the effect of processing condition on glass forming ability of BMGs. In this study, we have prepared CuZr-based BMGs at different casting temperatures. Increasing casting temperature increases glass forming ability and decreases the amount of the crystalline phase during BMG solidification. At a high casting temperature 1723 K, fully amorphous sample is obtained at a size of 2 mm in diameter. While under the lower casting temperatures (1523 K and 1323 K), crystalline CuZr phases exist. The formation of the crystalline phase is attributed to the initial crystals or cluster survived in the BMG melt during ingot remelting. The study indicates that casting temperature can be used as the controlling parameter to produce purely amorphous materials or crystalline CuZr-phase reinforced BMG composites, and the mechanical properties and thermal stability of the BMG composites can be tailored by the amount of the crystalline phase existed in the materials.

Introduction

Properties of materials depend on their microstructures, while the microstructures are closely correlated to the manufacturing processes used. Many processing methods, for example, quenching, annealing, cold working, etc., are developed to achieve the various desired microstructures, and then optimal material properties. Of which, melt treatment including ultrasonic vibration treatment [1] and superhigh temperature treatment [2], is evidence to be effective in changing the microstructures and improving the properties of Al-, Ni-, Fe-based alloys, and have been widely used in industrial production.

Metallic glass (MG) has been developed for almost 50 years [3]. Like the steel industry, the database among processes, microstructures and properties for bulk metallic glasses (BMGs) should be built up in order to promote their commercial production and applications. In the past few decades the researchers in this field have concentrated on exploring alloy compositions to obtain large glass forming ability in all common alloy systems [4-6]. Significant progress has been achieved, as seen by the successful development of BMGs in many alloy systems including Al, Fe, Ni, Cu, Zr, Mg, Re (rare earth metals) -based alloys. The size of BMGs has been increased from micron to inch [4-6], and the plasticity of BMGs has improved by introducing particle [7] and fiber [8] to form BMG composites. However, very few studies focus on BMG processing conditions. Shen et al [9] studied the effect of cooling rate on plasticity of TiCu-based BMG. Popel et al [2] reported the effect of quenching temperature on microstructures of Al and Fe-based ribbons. Improving the knowledge in this area will be crucial for BMGs production. In this study, we look at the influence of casting temperature on BMG glass forming ability, and investigate the relationship between the microstructures obtained under different casting temperatures and their mechanical properties.

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Experimental

Ingots with nominal composition of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ were obtained by arc-melting high purity elements under Ti-getter argon atmosphere. The ingots were remelted under vacuum in quartz tubes using an induction-heating coil and then injected into copper mould under a high purity argon atmosphere to receive the cylindrical rod samples. The casting temperature was monitored by an infrared thermoscope. Three casting temperatures were chosen, 1323 K, 1523 K and 1723 K, and the accuracy of the temperature control was estimated to be ± 10 K. The oxygen content of the samples fabricated under different temperatures was measured to be below 500 ppm. Amorphous ribbon samples with a thickness of about 60 μm were prepared by single roller melt-spinning method. The continuous differential scanning calorimeter (DSC) experiment of the rod samples and ribbon samples was performed on a Netzsch DSC 204 at a heating rate of 20 K/min. Microstructures were checked using X-ray diffraction (Cu Kα radiation), optical microscope and scanning electron microscope (SEM). Compression tests were performed to evaluate mechanical properties of the samples.

Results

In order to check the influence of casting temperature on glass formation in the $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy, the alloy was cast into 2 and 3-mm-diameter cylindrical samples under different casting temperatures of 1323 K, 1523 K and 1723 K. Fig. 1 shows their XRD patterns. Only the 2-mm-diameter samples prepared at 1723 K possesses a broad peak in the XRD patterns, indicating that the sample is in the amorphous state. The other two 2-mm-diameter samples cast at lower temperatures exhibit some Bragg peaks on XRD patterns. All 3-mm-diameter samples are clearly seen the Bragg peaks in their XRD patterns, showing they are crystallized to some extent. The crystalline phases formed during solidification were indexed as CuZr, maybe a mixture of austenite and martensite phases. It was found that the percentage of the crystalline phase reduces with the increase of casting temperature. This was further confirmed by the DSC measurement and microstructure observation.

Fig 2 shows DSC curves of 2-mm-diameter samples prepared at different casting temperatures. The onset crystallization temperature and crystallization enthalpy for these samples were determined. The value of the crystallization enthalpy (shown in Fig. 2) increases with increasing casting temperature. Using the ribbon quenched at 1723 K as reference for fully amorphous

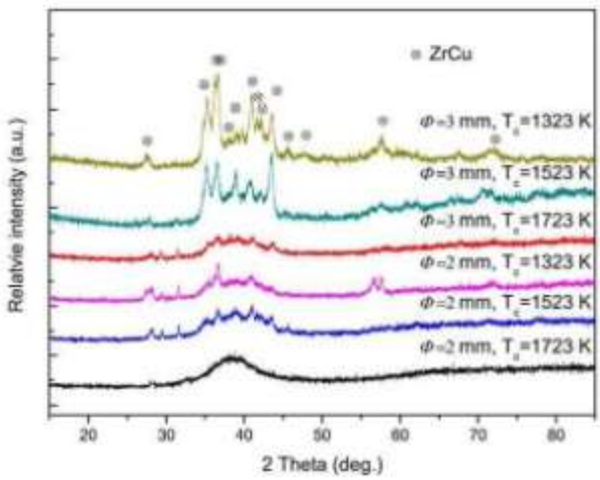

Fig. 1. XRD patterns of the rod samples cast at

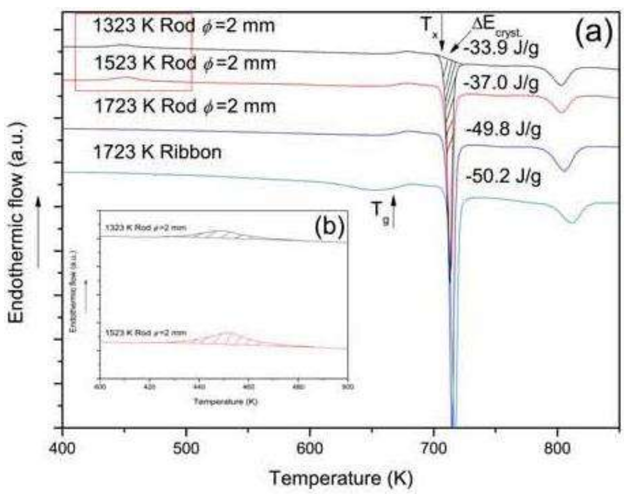

Fig. 2. DSC scanning of the 2-mm-diameter

different temperatures and different diameters.

rod samples. The DSC curve of ribbon sample is listed as reference. Fig. (b) is the high mag of the rectangle in (a).

state, we can calculate the content of the crystalline phase in the samples. The results are 32.5%, 26.3% and 0.8% for samples of 1323 K, 1523 K and 1723 K respectively. The content of crystalline phases falls with increasing casting temperature. When the casting temperature reaches 1723 K, almost no crystalline phase is formed.

For the 1323 K and 1523 K samples, some small endothermic peaks are observed in the range from 420 K to 470 K, which are magnified in Fig. 2b. Martensite transformation of the crystalline CuZr phase is thought to be responsible for these peaks [10]. No peaks are found for the sample prepared at 1723 K. This also suggests the sample prepared at 1723 K is amorphous. From these results, one may conclude that high casting temperature would enhance glass forming ability. It also implies that controlling casting temperature can be used to adjust the amount of crystalline phase in BMG matrix composites.

The morphologies of the crystalline phases in different samples are shown in Fig. 3. When the casting temperatures are 1323 K and 1523 K, the crystals are observed in the form of spheres (Fig. 3a and 3b). Most of crystalline phases are aggregated together, which may be due to the inhomogeneous distribution of cooling rate along the radial direction during casting. When the casting temperature elevates to 1723 K, no crystals are observed, as seen in Fig. 3c. The amount of

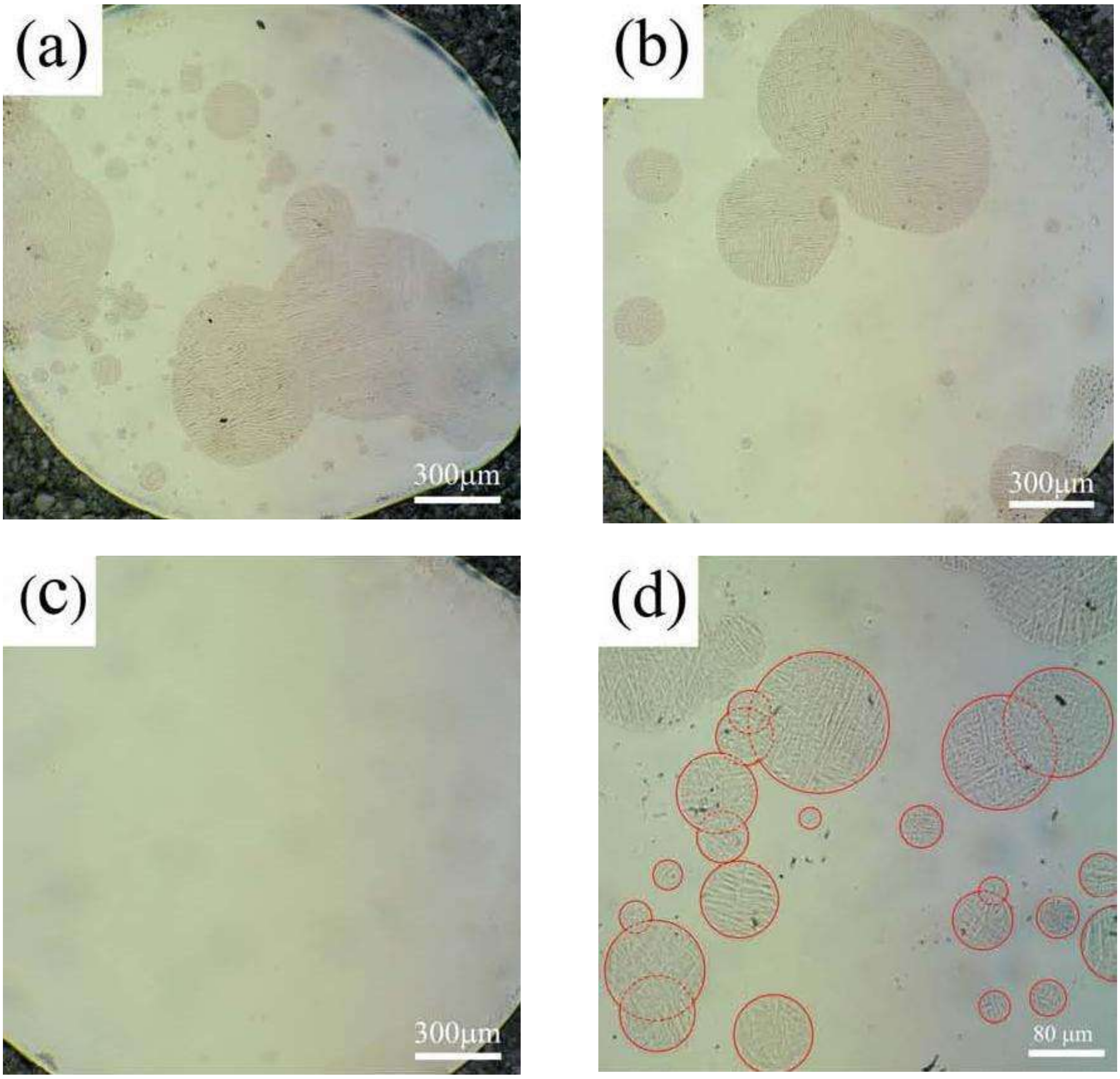

Fig.3. Optical images of rod samples prepared at different casting temperatures: (a) ∅2 mm, 1323 K; (b) ∅ 2 mm, 1523 K; (c) ∅ 2 mm, 1723 K; and (d) ∅1.5 mm, 1323 K.

the crystalline phases in samples with different casting temperatures is consistent with the XRD and DSC measurements. These results also support the conclusion that increasing casting temperature enhances glass forming ability of the alloy.

It is generally accepted that the introduction of second phase, such as fiber, dendrite, particle etc., into the amorphous matrix help to improve the properties of BMGs, especially plasticity, which is one of the principal restraints for BMGs' commercial applications [4-8]. In the present work, we also examined the effect of the precipitated crystalline CuZr phases on mechanical properties of samples using compression tests. The typical true stress-strain curves for the samples cast at different temperatures are shown in Fig. 4. The sample prepared at 1723 K yields at about 1600 MPa and immediately fractures at 1770 MPa with little plastic deformation (about 0.5%). For samples prepared at 1323 K and 1523 K, the yield strength falls to about 1100 MPa and 1220 MPa, respectively, followed by obvious work hardening. The materials fail at 1770 MPa and 1820 MPa respectively with plastic deformation of about 5% and 7% at fracture. Plasticity improvement was reported in other CuZr- [11-13] and TiCu- [14] based amorphous alloys. Multiple shear bands were believed to ductilize the BMG materials [15]. Fig. 4 also shows the compressive stress-strain curve of the 3-mm-diameter sample, which consists of large amount of CuZr phases as shown in Fig. 1. This sample exhibits an extraordinary work hardening, yielding at about 460 MPa and gradually increasing to about 1750 MPa with about 6% plastic deformation. As a result, we considered that CuZr phases formed at lower casting temperatures of 1323 K and 1523 K significantly improve mechanical properties of BMGs and are responsible for their work hardening ability.

Discussions

Casting temperature has a large influence on the glass forming ability of the alloy, as shown in Fig. 1. Generally, glass formation can always be correlated to its opposition process, which is nucleation and growth of crystals [4-6]. To obtain high glass forming ability, techniques avoiding crystallization in the melt is highly desirable. From XRD we identified that the primary competing crystalline phase against glass formation is CuZr phases in the present alloy. To better understand the crystallization process of CuZr phases, we observed the morphology of CuZr phases at higher magnification, as shown in Fig. 3d, and compared to Fig. 3a and b. The crystals are heterogeneously

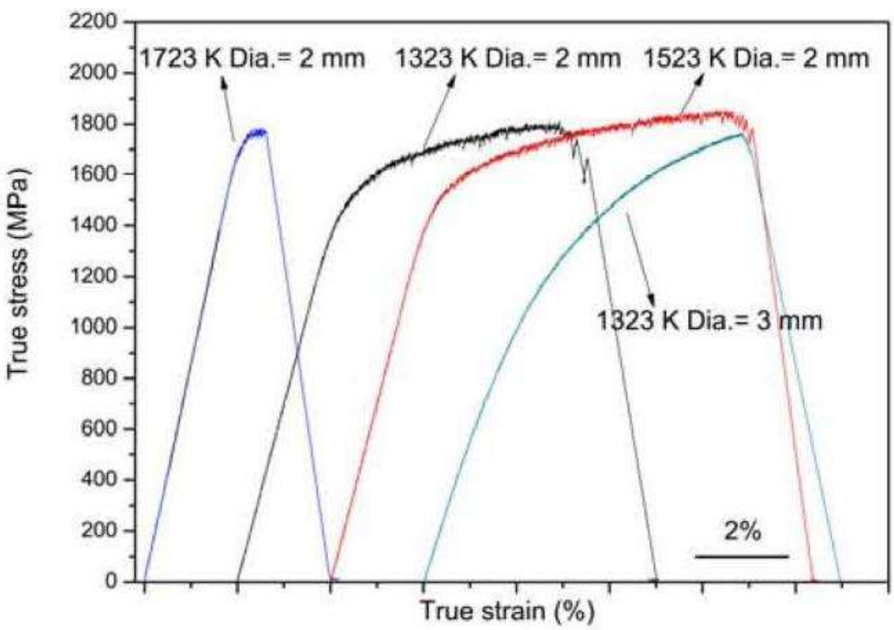

Fig. 4. Typical true stress-strain curves of the rod samples with different diameters and different casting temperatures.

distributed in the amorphous matrix whether on a macroscopic (Fig. 3a and b) or microscopic (Fig. 3d) scale. This sheds light on the formation mechanism of CuZr phases. Heterogeneous distribution of CuZr phases may be attributed to the following two reasons. Firstly, the inhomogeneous distribution of cooling rate along the radial direction, as mentioned above, which leads to the macroscopic inhomogeneity. The second is the occurrence of heterogeneity in the melt [2,16], which induces preferential nucleation and growth in some sites. These nuclei grow in the form of spheres, which is different from the growth mechanism of dendrites. With crystallization proceeding, the aggregation occurs, as marked in Fig. 3d. This accelerates the crystallization, which leads to the morphology of crystals shown in Fig. 3a and b.

The pre-existing nuclei in the melt results from melt heterogeneity can be two possible forms. One is the local ordering cluster, which is suggested to exist in the melt by previous literature [2,16]. The other one is surviving crystals after remelting, which can melt at ultrahigh temperature. Both are thought to be metastable and can gradually dissipate with the increase of temperature. When casting temperature is very high (1723 K in the present work), the heterogeneity in the melt would disappear and glass forming ability will be enhanced. It is consistent with the results we previously reported that the enhancement of thermal stability of amorphous was observed in the alloys prepared under high casting temperature [17]. While at low casting temperatures (1323 K and 1523 K in the present work), some crystals will precipitate.

Although the heterogeneity surviving in the melt under low casting temperature deteriorate glass forming ability of the alloy, the crystals phases grown up from those heterogeneity improve the mechanical properties of BMGs, as shown in Fig. 4. The samples with homogeneous amorphous structure obtained by high casting temperature exhibit brittleness, like most of BMGs. The CuZr phases formed in the samples prepared at low casting temperatures are softer and more ductile than the monolithic BMGs. Under loading, the CuZr phases will undergo plastic deformation at relatively low stress level while the amorphous matrix remains elastic. This kind of inconsistency of deformation behaviors between the amorphous matrix and CuZr phases leads to stress concentration on the interface. It is generally accepted that the in-situ formed CuZr crystals are well bonded with the glassy matrix, which avoids the initiation of the cracks on the interface. To keep the consistency of deformation behaviors between the amorphous matrix and CuZr phases, shear bands would be initiated in the amorphous matrix under further loading. This leads to the loss of yield strength in the materials, which is shown in Fig. 4. However, multiple shear bands initiating in the amorphous matrix can accommodate much plastic deformation, contributing to the improvement of plasticity of the materials.

In general, glass forming ability and property of BMGs are closely related to their solidification conditions. Controlling solidification conditions, for example casting temperature in the present work, provides a new method to further improve glass forming ability of the alloys. It can also be used for improving mechanical properties of BMGs by introducing structural heterogeneity on a macro- or nano-scale. Understanding the relationship between solidification conditions and properties of BMGs would be significant and beneficial to promote BMGs' applications.

Conclusions

The influence of casting temperature on microstructures and mechanical properties of $Cu_{50}Zr_{45.5}Ti_{2.5}Y_2$ alloy prepared using copper mold casting were investigated in the present work.

1. With the increase of casting temperature, glass forming ability of the alloy is enhanced. At the casting temperature of 1723 K, full amorphous sample was successfully made at a size of 2 mm in diameter. At the lower casting temperatures, CuZr phases were primarily precipitated in the alloy. It is thought to be attributed to the crystals or clusters surviving in the melt.

2. A CuZr-phase reinforced BMG matrix composite with good mechanical properties was prepared. The amount of CuZr phases is related to the casting temperature. Mechanical tests indicate that CuZr phases are softer and more ductile than the amorphous matrix. Under loading, CuZr phases induce the initiation of multiple shear bands, leading to large improvements in the plasticity of the materials.
3. The BMG composites with crystalline CuZr phases exhibit significant work hardening in the compression tests, which is attributed by the precipitated CuZr phases.

Acknowledgments

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