Eutectic crystallization behavior of new Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy with high glass-forming ability

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Abstract. A water quenching method is used to produce as-cast Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ rods with diameters from 20 mm to 25 mm. The microstructures of the as-cast samples were investigated by X-ray diffraction, optical microscopy and scanning electron microscopy. Furthermore, the crystallization behavior of the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ glassy alloy was examined by XRD and transmission electron microscopy. Based on the results obtained one can assume that the simultaneous precipitation of the Zr$_2$Cu+AlCu$_2$Zr eutectic phases is the possible reason for the high stabilization of the quaternary Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ supercooled liquid.

1. Introduction
Due to their scientific interests and engineering significance, bulk metallic glasses (BMGs) have attracted great attention in recent years. During the past two decades, BMGs have been developed in a number of alloy systems, for example, multicomponent Zr-based, Mg-based, La-based, Pd-based and Fe-based alloy systems et al. [1]. The critical sizes of these alloys for glass-formation range from several millimetres to several centimetres. Glass-forming ability (GFA) is one of the most important subjects in the research field of BMGs, because it determines the potential for the BMGs to be utilized in various applications. In order to effectively predict GFA and pinpoint the alloy composition with high GFA, great efforts have been made to investigate the theoretical and empirical descriptions of GFA [1-3]. Turnbull’s early work [2] on nucleation suggested that as the ratio of the glass-transition temperature to the liquidus temperature of an alloy increases, the homogeneous nucleation of crystals in the undercooled melt should become much more sluggish. Accordingly, the glass formation is always associated with deep-eutectic composition [2, 3]. This “Turnbull” criterion for the suppression of crystallization in undercooled melts remains today one of the best “rules of thumb” for predicting the GFA of any liquid.

Recently, we developed a new series of Zr-Cu-based BMGs with high GFA in Zr-Cu-Al-Ag alloy system [4], in which the representative Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy was found to have a large critical diameter of 25 mm for glass-formation. Moreover, the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy shows a single-event feature on its melting curve, indicating that the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy is located at a quaternary Zr-Cu-Al-Ag eutectic point. The high GFA of the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy has been considered to result from the high stability of the undercooled melt [4, 5]. Since the structural characteristics of the precipitated crystalline phases are closely related to the stability of the undercooled liquid, the understanding of the crystallization behavior of the undercooled Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ liquid will contribute to the clarification of the glass-formation mechanism and the development of new BMGs with high GFA in Zr-Cu-based alloy system. Thus, in the present paper we perform a systemic study on the crystallization behavior of the undercooled Zr$_{48}$Cu$_{36}$Ag$_8$Al$_8$ melt and the glassy Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy.

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The GFA is also analyzed based on the classical nucleation principles.

2. Experimental methods

The ingot of the Zr₄₈Cu₃₆Al₈Ag₈ alloy was prepared by arc-melting mixtures of Zr, Cu, Al and Ag in a high purity argon atmosphere. Bulk cylindrical rods with diameters from 10 mm to 25 mm were prepared by melting of the master ingots in sealed quartz tubes followed by water quenching. Ribbon sample was prepared by melt spinning. The glassy ribbons encapsulated in quartz tube under a vacuum were isothermally annealed in the supercooled liquid region, and then were quenched into water. The structure of the as-cast and annealed ribbon samples was examined by X-ray diffraction (XRD) using Cu-Kα source. The microstructure of the bulk samples was examined by optical microscopy (OM) and scanning electron microscopy (SEM). The morphologies of the annealed samples were investigated by a transmission electron microscopy (TEM).

3. Results and discussion

3.1 Solidification behavior of the undercooled melt

Figure 1 shows the XRD patterns of the as-cast alloy rods with diameters of 20 and 25 mm prepared by water quenching, together with the result of the ribbon sample. Consistent with the ribbon sample, the pattern of the rod with a diameter of 20 mm consists of only a broad diffraction maximum without any detectable sharp Bragg peaks, indicating that this rod is amorphous. As the sample diameter increases from 20 mm to 25 mm, the phase solidified from the melt is changed from the amorphous structure to the (tI₆)CuZr₂ + (cF₁₆)AlCu₂Zr + (tI₆)AgZr₂ phases, which are demonstrated by the XRD patterns in Fig. 1.

![Figure 1. XRD patterns of the as-cast Zr₄₈Cu₃₆Al₈Ag₈ rods with diameters of 20 and 25 mm prepared by water quenching and the ribbon sample prepared by melt spinning.](image)

To identify the microstructure of the rod with a diameter of 25 mm, OM and SEM were employed and the micrographs are shown in Fig. 2. At a low magnification (Fig. 2 (a)), equiaxed grains with size of 1-3 mm impinging on one another are observed in the cross section of the 25-mm rod. Moreover, it is seen that the grains are composed of a lot of radial dendrites. Fig. 2 (b) and (c) present the SEM micrographs of the equiaxed grains with larger magnifications. As shown in Fig. 2(b), the radial dendrites in equiaxed grain consist of the Zr₂Cu+AlCu₂Zr cellular eutectics (The phases were identified by an X-ray energy dispersive spectroscopy), which exhibit a regular lamellar morphology. Thus, the equiaxed grain is actually a kind of equiaxed eutectic. Consistent with the result of the DTA, the form of the solidification microstructures confirms that the Zr₄₈Cu₃₆Al₈Ag₈ alloy is located at a
Zr₂Cu+AlCu₂Zr eutectic point. In addition, as shown in Fig. 2(c), a small number of lump AgZr₂ phases precipitate along the boundary of the Zr₂Cu+AlCu₂Zr cellular eutectic. In light of the observed microstructures and identified crystalline phases, the solidification of the Zr₄₈Cu₃₆Al₈Ag₈ undercooled melt under water quenching condition would proceed as follows: (1) when the diameter of the rod is equal to or less than 20 mm, the undercooled melt will directly solidify into the glassy phase; (2) when the diameter of the rod is 25 mm, the Zr₂Cu+AlCu₂Zr eutectic seeds will start in the melt, and the eutectic grains then continue to grow in an essentially spherical form. Moreover, the AgZr₂ phases precipitate from the last residual liquid containing excess solutes rejected by the eutectic phases and distribute at the boundaries of the eutectic cells or dendrites.

The high GFA of the Zr₄₈Cu₃₆Al₈Ag₈ alloy has been found to be related with the high stabilization of supercooled liquid, which is represented by a large value of ΔTₜ, of about 101 K and a low melting temperature of 1143 K [4]. It has been proposed that formation of a unique glassy structure with highly dense random packing owing to negative heats of mixing and large atomic size mismatches among the constituent elements should be mainly responsible for the high GFA of the Zr₄₈Cu₃₆Al₈Ag₈ alloy [4, 5]. In the current work, the microstructure observations (Fig. 2) of the water-quenching samples suggest that the Zr₄₈Cu₃₆Al₈Ag₈ alloy is located nearly at Zr₂Cu+AlCu₂Zr eutectic point. As compared with the composition of the master alloy, the Zr₂Cu phase shows higher content of Zr, and the AlCu₂Zr phase contains higher content of Al and Cu. In order to form the Zr₂Cu+AlCu₂Zr eutectic, a significant mass redistribution must be provided to produce simultaneously both solid phases, which form with a periodic interlameller spacing λ in the Zr₄₈Cu₃₆Al₈Ag₈ undercooled melt [6, 7]. On the contrary, the Zr₄₈Cu₃₆Al₈Ag₈ undercooled melt exhibits a highly dense random packing structure [4, 5], which can effectively slow down the mass redistribution. Therefore, high GFA of the Zr₄₈Cu₃₆Al₈Ag₈ alloy should result from the suppression of the competing Zr₂Cu+AlCu₂Zr eutectic phases through controlling the mass redistribution by the high stabilization of the undercooled liquid. Similar to the Zr₄₈Cu₃₆Al₈Ag₈ alloy, the Zr₄₄Ti₁₄Cu₁₂Ni₁₀Be₂₃ alloy with high GFA also shows a multiphase eutectic microstructure at low cooling rate [8]. Although the identification of the eutectic phases for the Zr₄₄Ti₁₄Cu₁₂Ni₁₀Be₂₃ alloy has not been made clear due to the complexity of the multicomponent alloy, the similar solidification mode for these two alloys indicates that to find a eutectic point is a key for the development of the Zr-based alloys with high GFA.

3.2 Crystallization behavior of the glassy alloy

Previous work [4] showed that the glassy Zr₄₈Cu₃₆Ag₈Al₈ alloy exhibits a large temperature interval of the supercooled liquid region ΔTₜ, of 101 K (ΔTₜ= Tₜ₊₁−Tₜ₋₁= 791−690= 101 K, Tₜ: the onset temperature of crystallization; Tₜ₊₁: the glass transition temperature). In the present work, we annealed the glassy Zr₄₈Cu₃₆Ag₈Al₈ ribbon in the supercooled liquid region at 740 K and 773 K, respectively, for 1800 seconds. Figure 3 shows the XRD patterns of the annealed ribbon samples. As shown in Fig. 3, the sample annealed at 740 K exhibits the same diffraction peaks, which are indexed as the (tl₆)CuZr₂, (cF₁₆)AlCu₂Zr, (hP₁₂)Al₁₂Zr, (tP₄)AgZr phases and some unknown phases, as the sample annealed at 773 K except for lower intensity. This indicates that the same crystalline phases precipitate from the
supercooled liquid region in a wide range of annealing temperature. The microstructure of the ribbon samples annealed at 740 K and 773 K is shown in Fig. 4. As shown in Fig. 4(a), the spherulitic particles with size ranges from 5 to 15 nm distributed in the glassy matrix can be observed in the sample annealed at 740 K. The selected-area electron diffraction (SAED) pattern in Fig. 4(a) also demonstrates the coexistence of the nanocrystalline phases together with the glassy phase. However, a higher annealing temperature results in a different microstructure morphology. As shown in Fig. 4(b), the dominate observation in the sample annealed at 773 K is the inner flower-like spherulites of about 500 nm large, which are the Zr$_2$Cu+AlCu$_2$Zr eutectics. Besides, a number of nanocrystalline phases with size of about 20 nm are observed along the boundary between the spherulites. Devitrification mechanisms of metallic glasses are generally divided into four categories: polymorphous, eutectic, primary and devitrification with phase separation. From these measurements, it is found that crystallization mechanisms of the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ glassy alloy changes from the primary crystallization mode to the eutectic crystallization mode with increasing annealing temperature.

As compared with the solidified phases from the undercooled melt, much more crystalline phases precipitated from the supercooled liquid for the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ glassy alloy. This should be due to the pronounced asymmetry in the crystallization behavior during heating and cooling for the metallic glass-forming liquid [9]. However, the Zr$_2$Cu and AlCu$_2$Zr phases are the main structure constituents for the annealed glassy samples, similar to the water-quenching sample. And, the higher annealing temperature leads to the formation of the Zr$_2$Cu+AlCu$_2$Zr eutectic phase. It has been reported that the single Cu$_{10}$Zr$_7$ phase precipitates as the main crystalline phase from the annealed ternary Zr-Cu-Ag glassy alloys with low GFA [10], which is significantly different from the quaternary Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy. Therefore, it is concluded that the simultaneous precipitation of the Zr$_2$Cu and AlCu$_2$Zr phases should be the reason for the high stabilization of the quaternary Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ supercooled liquid.

4. Conclusion
The Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ alloy can form a glassy rod with a diameter of 20 mm using a water quenching method. As the sample diameter increases from 20 mm to 25 mm, the phase solidified from the melt is changed from the amorphous structure to the Zr$_2$Cu+AlCu$_2$Zr eutectic with a small number of Ag$_2$Zr phase. As compared with the solidified phases from the undercooled melt, much more crystalline phases, including the CuZr$_2$, AlCu$_2$Zr, Al$_2$Zr, AgZr phases and some unknown phases, precipitated from the Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ glassy alloy annealed in supercooled liquid region. The higher annealing temperature leads to the precipitation of the Zr$_2$Cu+AlCu$_2$Zr eutectic phase from the annealed glassy alloy as the main structure. The simultaneous precipitation of the Zr$_2$Cu and AlCu$_2$Zr phases should be responsible for the high stabilization of the quaternary Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ supercooled liquid.

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