

Spheroidization behavior of dendritic b.c.c. phase in Zr-based β -phase composite

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Abstract: The spheroidization behavior of the dendritic b.c.c. phase dispersed in a bulk metallic glass (BMG) matrix was investigated through applying semi-solid isothermal processing and a subsequent rapid quenching procedure to a Zr-based β -phase composite. The Zr-based composite with the composition of $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$ was prefabricated by a water-cooled copper mold-casting method and characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results show that the composite consists of a glassy matrix and uniformly distributed fine dendrites of the β -Zr solid solution with the body-centered-cubic (b.c.c.) structure. Based on the differential scanning calorimeter (DSC) examination results, and in view of the b.c.c. β -Zr to h.c.p. α -Zr phase transition temperature, a semi-solid holding temperature of 900 °C was determined. After reheating the prefabricated composite to the semi-solid temperature, followed by an isothermal holding process at this temperature for 5 min, and then quenching the semi-solid mixture into iced-water; the two-phase microstructure composed of a BMG matrix and uniformly dispersed spherical b.c.c. β -Zr particles with a high degree of sphericity was achieved. The present spheroidization transition is a thermodynamically autonomic behavior, and essentially a diffusion process controlled by kinetic factors; and the formation of the BMG matrix should be attributed to the rapid quenching of the semi-solid mixture as well as the large glass-forming ability of the remaining melt in the semi-solid mixture.

Key words: bulk metallic glass composite; semi-solid isothermal processing; spheroidized microstructure

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Bulk metallic glasses (BMGs) have shown unique mechanical properties such as superior strength and hardness, excellent corrosion and wear resistance^[1-5]. However, their plastic deformation is localized in narrow shear bands, followed by the rapid propagation of these shear bands and sudden fracture. Such a deformation behavior results in their apparent brittle failure at room temperature and significantly hinders their application as structural parts^[6-8]. One effective way to improve the ductility of BMGs is to control the initiation and propagation of shear bands^[9, 10]. Specifically, through manipulating the microstructure, the shear band behavior can be well controlled. The β -phase composites become

potential candidate materials to validate this method. The first such composite, $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$, developed by Kim et al., consists of a glassy matrix with embedded micrometer sized b.c.c. β -Zr (Ti, Nb) dendrites, and is usually called the " β -phase composite"^[11]. The ductile β -phase is formed by the nucleation and the dendritic growth process upon cooling of the melt. Therefore, it's the microstructure of β -phase, specifically the morphology, the size and the volume fraction can be intentionally tailored by controlling the solidification process^[11, 12].

We developed a unique processing method to achieve the desired microstructures so as to enhance the mechanical properties in Zr-based β -phase composites, which was based on controlling solidification in the liquid-solid two-phase region^[13]. As a result, a novel microstructure with dispersed micro-sized spherical β -phase particles in a BMG matrix was obtained. Room temperature compression tests showed that the yield stress and plastic strain of the composite with the spherical β -phase particles were about 1,350 MPa

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and 12%, respectively; against 1,208 MPa and 8.82% for a composite of similar composition and volume fraction of crystals, but with dendritic β -phase inclusions^[14]. Furthermore, based on controlled solidification combined with composition optimization, we developed another Zr-based β -phase composite which contains high volume fraction of coarsened β -phase with a nearly spherical morphology and displays a large fracture strain up to 22.3% under uniaxial compression at room temperature^[15].

In the last few years, there has been increasing interest in developing BMG composites containing coarsened, ideally spheroidized, crystalline inclusions. In 2008, Hofmann et al. reported Zr-based BMG composites with both high toughness and tensile ductility, which were developed through modifying alloy composition and treating the molten alloys in their semi-solid two-phase region^[6]. More recently, a process combining cooling slope casting and suction casting was developed to generate a semisolid structure in a Zr-based BMG composite. As a result, a structure consisting of a glassy matrix with dispersed spheroidal and rose-like β -Zr b.c.c. phase crystals was obtained^[16]. Moreover, an in-situ formed spherical intermetallic particles/BMG matrix composite with high strength and good plasticity has been fabricated through the casting of Zr-based alloy melts^[17]. In 2010, another fabrication method was also developed to produce spherical crystalline particles in the amorphous matrix, based on the mechanism of the liquid-liquid phase transformation in the miscibility gap of the multi-component immiscible alloy^[18]. Nevertheless, most BMG in situ composites reported so far contain dendritic inclusions rather than spherical particles. Coarsening the spherical b.c.c. β -Zr particles becomes a potential solution to improving the mechanical properties of Zr-based β -phase composites^[13-15]. So attempts to spheroidize the dispersed b.c.c. β -phase dendrites in a BMG matrix by simple processing are meaningful.

In this paper, a complete spheroidization processing has been designed and applied to the Zr-based BMG matrix composite with the typical composition of $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$, which contains b.c.c. β -phase dendrites. As a result, the desired microstructure composed of a BMG matrix and uniformly distributed spherical β -phase particles with a high degree of sphericity has been achieved. The details of the establishment of the semi-solid isothermal technique are presented below.

1 Experimental details

1.1 Synthesis

Master alloy ingots with a nominal composition of $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$ (atomic percent) were prepared by arc melting the mixture of pure Zr (99.95 mass%), Ti (99.95 mass%), Nb (99.95 mass%), Cu (99.99 mass%), Ni (99.95 mass%), and Be (98.5 mass%) metals under a Ti-gettered argon atmosphere in a water-cooled copper crucible. After mechanical grinding, the master alloy ingots were crushed into pieces and then placed in a quartz tube in a vacuum of 4×10^{-3} Pa. Plate-shaped samples with approximate dimensions of 50 mm \times 50 mm \times 3 mm were

prefabricated by induction-melting these small master alloy pieces and then casting the molten alloy into a water-cooled copper mold. Thus the prefabricated plate samples with an initial microstructure were obtained. Strips of appropriate dimensions were cut from these prefabricated plates using a wire cutting machine and then encapsulated in quartz tubes with an 8 mm inner diameter and a vacuum of 4×10^{-3} Pa. The spheroidization processing was carried out by reheating the encapsulated alloy strips to the designed temperature, followed by an isothermal holding process at this temperature for 5 min in a resistance furnace, and then quenching them into iced-water.

1.2 Characterization

The phase analysis of the samples was performed using a Rigaku D/max 2038 X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 0.154$ nm). The morphology and dispersed state of the crystalline phase were observed using a JSM-6700F field emission scanning electron microscope (SEM) at 15 kV. The chemical compositions were determined using an electron microprobe (EPMA) attachment on the JEOL SEM. NETZSCH DSC 204 differential scanning calorimeter (DSC) was used to characterize the glass transition, crystallization and the melting behavior of the prefabricated material, with a heating rate of 20 K \cdot min $^{-1}$.

2 Results and discussion

2.1 Initial as-cast microstructure

Figure 1 shows the SEM micrograph of a polished and chemically etched cross section of the prefabricated plate-shaped samples. As an initial microstructure, it can be seen from this figure that dendrites with an average size of about 10 – 20 μ m are homogeneously dispersed in a dark matrix. The insert is the XRD pattern of the initial microstructure, which shows sharp peaks superimposed on a broad scattering hump characteristic of an amorphous phase. The diffraction peaks located at $2\theta = 36.24^\circ$, 52.04° and 65.43° can be indexed as (110), (200) and (211) of the β -Zr phase with a body-centered-cubic structure (b.c.c.). No other phases are detected within the sensitivity limit of the XRD. Taking $\lambda = 0.154$ nm of the Cu K α radiation, the lattice parameter of the b.c.c. structure is estimated to be 0.3489 nm from the strongest (110) peak. EPMA analysis shows that the average composition of the β -phase is $Zr_{64.66}Ti_{15.40}Nb_{15.14}Cu_{2.90}Ni_{1.90}$, indicating the main solute elements contained in the β -Zr solid solution are Ti and Nb. These results demonstrate that a Zr-based in situ β -phase composite with fine b.c.c. β -Zr (Ti, Nb) dendrites has been obtained.

Upon continuous cooling from a homogeneous high temperature melt, the present Zr-based alloy undergoes partial crystallization by nucleation; and subsequent dendritic growth of the b.c.c. β -Zr solid solution. This shifted the composition of the remaining liquid to a composition that is close to Vit. 1 ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$), one of the most successful BMG alloys. Subsequently, the remaining melt freezes to a glassy state and the two-phase microstructure composed of the

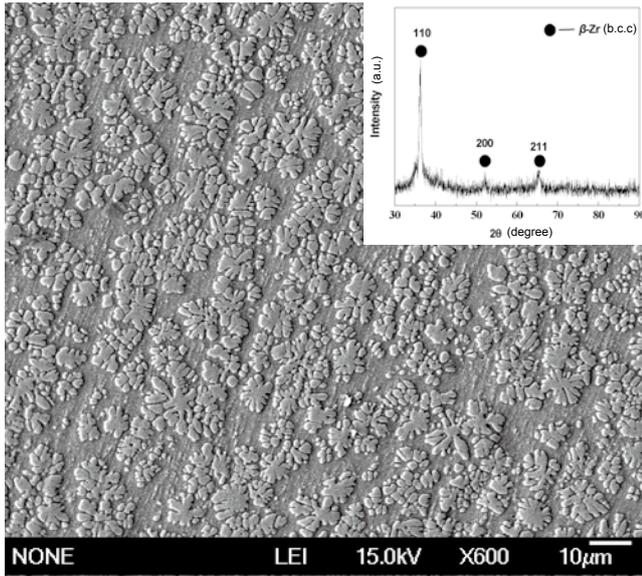


Fig. 1: SEM micrograph of initial as-cast microstructure obtained from the prefabricated Zr-based in situ composite with a composition of $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$, showing dispersed fine dendrites in a dark matrix. (Insert: X-ray diffraction pattern for the initial microstructure showing three main peaks of the b.c.c. β -Zr phase superimposed on a broad scattering feature characteristic of an amorphous phase).

dispersed β -phase dendrites in the glassy matrix was formed. Here, the element Nb stabilizes the ductile b.c.c. phase over the h.c.p. α -Zr (Ti, Nb) phase [11, 19].

2.2 Spheroidization mechanism

Because of the existence of a large interface between phases, the present dendritic β -phase/BMG matrix two-phase system is not initially in thermodynamic equilibrium. Its total energy can be decreased via a change in the morphology and/or an increase in the size scale of the β -phase, thus causing a decrease in total interfacial area. Such a process is often called Ostwald ripening.

The driving force for the Ostwald ripening process is the well-known curvature dependence of the chemical potential which, assuming isotopic surface energy, is [20]

$$\mu = \mu_0 + V_m \gamma k$$

where μ_0 is the chemical potential of an atom at a flat interface, V_m is the molar volume, γ is the isotropic surface energy and k is the mean interfacial curvature. This functional relationship implies that, for a two-phase mixture composed of a dispersed second phase in a matrix, atoms of the second phase will tend to flow from regions of high curvature to regions of low curvature; which is consistent with the necessary decrease of total energy in the two-phase system and will result in the disappearance of surfaces possessing high curvature and an increase in the size scale of the second phase itself. As a limiting state, the dispersed second phase will transform into coarse spherical particles.

For the present b.c.c. β -phase dendrite dispersed in the BMG matrix, the curvature at different positions might

be different. Thus, its spheroidization by an atom flow is thermodynamically autonomic behavior. However, because the atom flow is essentially a diffusion process controlled by kinetic factors, a high enough temperature and/or enough time would be necessary conditions for the completion of the rounding transition of the β -phase.

2.3 DSC results and analysis

Figure 2 shows the DSC curve of the fabricated β -phase composite. T_g and T_{x1} , marked with arrows, represent the onset temperatures of the glass transition and first crystallization event, at about 605 and 646 K, respectively. Thus, the super-cooled liquid region (ΔT_x) defined by the difference between the T_g and T_{x1} is 41 K. Further, the DSC curve demonstrates that the composite's glassy matrix starts to melt at the temperature 923 K marked with the arrow T_m , followed by complete melting at 937 K marked with T_l . The existence of a small melting interval of only 14 K between the T_m and T_l means that the composition of the glassy matrix is very close to a eutectic composition. Taking $T_g = 605$ K and $T_l = 937$ K, the reduced glass transition temperature T_{rg} , defined by $T_{rg} = T_g/T_l$, is 0.65.

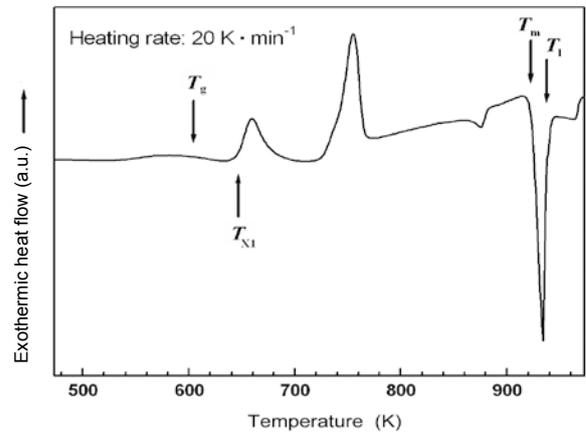


Fig. 2: DSC curve for as-cast Zr-based β -phase composite with a composition of $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$

It was believed that the wide super-cooled liquid region ΔT_x represents a high resistance to nucleation and growth of crystalline phases in the super-cooled liquid, and high T_{rg} values contribute to a higher glass-forming ability (GFA) [21, 22]. Also, it is generally believed that deep eutectics are the most favorable regions to obtain higher GFA, because $T_{rg}(T_{rg} = T_g/T_l)$ is high at this region [23]. Thus, the DSC scanning results reflect that the matrix material of the investigated composite has large thermal stability against crystallization. This is important for ensuring the glassy feature of the matrix in the final spheroidized microstructure.

2.4 Establishment of spheroidization processing

According to the microstructure-forming principle and the

spheroidization mechanism described earlier, as well as the results obtained by the DSC; reheating the prefabricated β -phase composite to a temperature just over the complete melting temperature of its matrix material, allows a semi-solid two-phase mixture consisting of dispersed β -phase dendrites in a liquid matrix to be obtained. Then, after isothermal holding of the two-phase mixture at this temperature for a sufficient time, followed by a rapid enough quenching, these dendrites would be spheroidized at the same time as the liquid matrix would be vitrified. Therefore, the desired microstructure composed of spherical β -phase particles in the BMG matrix would be achieved.

Based on the above analysis, the entire designed spheroidization processing is shown in Fig. 3. Here, the lower broken line corresponds to the complete melting temperature of the matrix $T_1 = 937$ K while the upper one represents the phase transition temperature 1,136 K below which the transformation from the present ductile b.c.c. β -Zr to a hexagonal close packed (h.c.p.) α -Zr phase might occur. Such a transformation is undesirable for the present spheroidization processing because the resulting h.c.p. structure has a worse ductility than its parent phase. Thus, the isothermal holding temperature was determined to be 1,173 K which is slightly higher than the phase transition temperature, but should not be too high. Higher than 1,173 K, a relatively wide semi-solid two-phase region will still exist after the spheroidization process, and thus some amount of dendritic β -phase may be retained in the final microstructure, which precipitate from the remaining semi-solid mixture and then grow in dendritic form during the following rapid quenching. This would produce an imperfectly spheroidized microstructure containing spheroidal and also dendritic β -phase. As to the 5 min holding time, this was determined in our previous works^[13-15].

2.5 The spheroidized microstructure

The designed spheroidization processing procedure is displayed in Fig. 3. The spheroidized microstructure and its XRD pattern are shown in Fig. 4. The insert is the XRD pattern of this

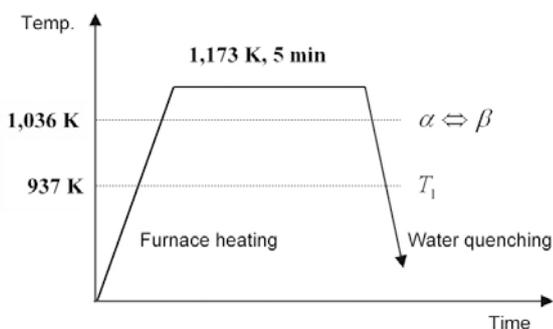


Fig. 3: Designed spheroidization process for Zr-based BMG in situ composite containing β -phase dendrites (Here, the lower broken line corresponds to the complete melting temperature of the matrix material; the upper one representing the phase transition temperature, below which an equilibrium transition from b.c.c. β -Zr (Ti, Nb) to h.c.p. α -Zr (Ti, Nb) might take place.)

microstructure. It can be seen that this XRD pattern is very similar to that of the initial microstructure shown in Fig. 1 in profile, implying that both of the microstructures have the same phase constitution. Namely, there is no h.c.p. α -Zr (Ti, Nb) phase existing in the spheroidized microstructure. These β -phase inclusions show regular spheroidal forms rather than dendritic structures. Their average size was estimated to be about 6 – 8 μm . These results indicate that the present spheroidization processing parameters, heating temperature 1,173 K and holding time 5 min, are appropriate. Meanwhile, the formation of the glassy matrix should be attributed to the subsequent rapid quenching of the semi-solid mixture as well as the large glass-forming ability of the remaining melt in the semi-solid mixture.

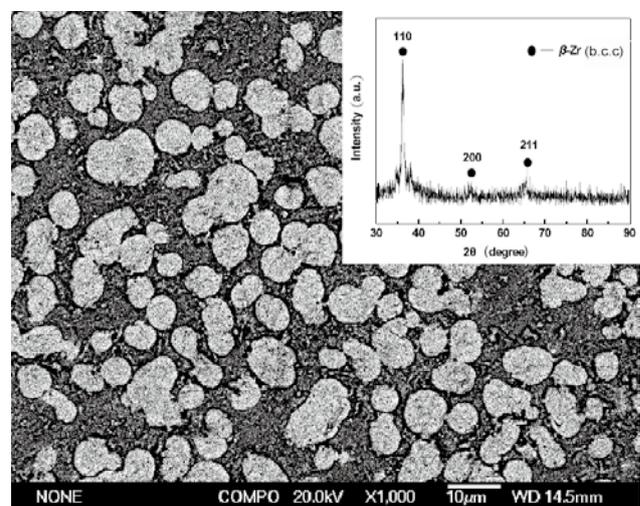


Fig. 4: SEM image of spheroidized microstructure showing uniformly distributed spheroidal particles in a dark matrix (Insert: X-ray diffraction pattern for the spheroidized microstructure showing a profile similar to that of the insert shown in Fig. 1.)

3 Conclusions

The two-phase microstructure composed of a BMG matrix and uniformly distributed spherical b.c.c. β -Zr particles with a high degree of spheroidicity can be achieved by applying a simple spheroidization processing to a Zr-based BMG composite containing in situ formed dendritic β -phase. The spheroidization processing involves a semi-solid isothermal holding process and the subsequent rapid quenching procedure to freeze the remaining liquid of the semi-solid mixture into a glassy state. 1,173 K is an appropriate isothermal processing temperature for the present spheroidization processing, as it is slightly higher than the phase transition temperature of the ductile b.c.c. β -Zr to h.c.p. α -Zr phase, but should not be too high. In the case of a higher processing temperature, a relatively wide semi-solid two-phase region would still exist after the spheroidization processing; resulting in an imperfectly spheroidized microstructure. The present spheroidizing behavior can be thermodynamically explained in terms of the curvature dependence of the chemical potential.

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