Cooling rate effects on the microstructure and phase formation in Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3} bulk metallic glass

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Abstract

A detailed transmission electron microscope (TEM) study has been conducted to investigate the microstructures of the Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3} metallic glass formed at different cooling rates. It has been found that the most competitive crystalline phase to the amorphous structure is an oxygen-stabilized FCC NiZr\textsubscript{2}-type phase, which in turn acts as the leading phase to trigger the formation of other crystalline phases in the slow-cooled alloy.

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1. Introduction

The study of in situ formed crystalline phases is important for bulk metallic glasses (BMGs) for two main reasons: Firstly, the knowledge of how and when crystalline phases form is vital to achieve defined composites (amorphous matrix with primary crystalline phases), which show greatly improved mechanical properties, such as plasticity; examples are shown in Zr-based \cite{1} and Ti-based \cite{2} BMGs. Secondly, knowledge of the crystalline phases competing with the desired amorphous structure is essential for designing the alloy compositions so as to obtain better BMG candidates.

The formation of crystalline phases in BMGs can be affected by several factors, namely the cooling rate \cite{3}, the composition (including impurity) \cite{4,5} and the processing conditions \cite{6,7}. Among them, the cooling rate is believed to be the most decisive one. For examples, Zhang et al. \cite{8} showed that different cooling rates could result in significant different crystalline phases and/or microstructures, from a unique amorphous structure to complicated composites, in a La-based BMG-forming alloy; and Loser et al. \cite{9} studied the cooling rate effects on the microstructure development of a Zr–Nb–Cu–Ni–Al BMG-forming alloy.

In this study, we investigate microstructures of a Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3} BMG \cite{10} prepared by different cooling rates. Since traces of oxygen (500 ppm) were detected in the studied alloy system, the relationship between the impurity and the phase formation is discussed based on the microstructural analysis.

2. Experimental procedure

Rod-shaped samples of \Phi 3, \Phi 5 and \Phi 10 mm with the nominal composition of Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3} were prepared by non-consumed arc melting and the copper mould casting technique under the protection of argon atmosphere. Based on a rough relationship between the cooling rate \( r \) (K/s) and the diameter \( d \) of the rod-shaped samples, i.e. \( r \sim 10/d^2 \) \cite{11}, the cooling rates of these three alloys can be estimated as 100, 40 and 10 K/s for the \Phi 3, \Phi 5 and \Phi 10 mm alloys, respectively. Thermal analysis was performed on a NETZSCH STA 409 CD with a heating rate of 0.167 K/s. The X-ray diffraction (XRD) experiments were conducted on a D/max IIIA X-ray
diffractometer with a Cu-Kα target operating at 40 kV and 60 mA. Microstructure investigations using scanning electron microscope (SEM) and transmission electron microscope (TEM) were carried out in a Philips XL30 (operated at 20 kV), a JEOL 6460 LV (operated at 20 kV) and a Tecnai F20 (operated at 200 kV), respectively. Energy dispersive spectrometers (EDS) attached to the SEM and TEM were used to provide compositional information. TEM specimens were prepared by the tripod technique, finished by a low-angle (<6°) and a low-energy (3.5 keV) ion-beam thinning to avoid the possible induced crystallization during the TEM specimen preparation. In order to determine the lattice parameters of crystalline phases accurately when using the selected area electron diffraction (SAED), pure gold nanoparticles were sputtered on the top of the TEM specimens in order to calibrate the camera length of the TEM. Oxygen measurement was performed using a Leco TC-436 type oxygen/nitrogen determinator, which detected a 500 ppm content of oxygen in all alloys.

3. Experimental results

3.1. XRD and thermal analyses

Fig. 1 shows XRD patterns of all three alloys. The XRD pattern taken from the φ3 mm alloy shows a broad diffuse halo with no other diffraction peaks, indicating that the amorphous structure is dominating the φ3 mm alloy. For the φ5 mm alloy, small peaks superimposed on the diffuse halo can be seen, suggesting that a certain degree of crystallization has taken place. The calculation of the reduced crystallization enthalpy, obtained from the thermal analysis \( V_f = \frac{\Delta H_a - \Delta H_c}{\Delta H_a} \), where \( V_f \) is the volume fraction of the crystalline phase(s), \( \Delta H_a \) is the crystallization enthalpy of the pure amorphous alloy which is determined via measuring the exothermal peak of the DSC curve and \( \Delta H_c \) is the crystallization enthalpy of the partial crystallized alloy, see [12] for details) shown in Fig. 2, determines an approximately 12% volume fraction occupied by the crystalline phase(s).

Compared with the φ3 and φ5 mm alloys, the φ10 mm alloy is well crystallized as evidenced by two key facts. Firstly, the shape of diffraction peaks shown in Fig. 1 indicates that crystalline phases have been well developed in the slow cooled solidification process. Secondly, although the thermal analysis detects a change in the heat flow around the temperature of 520 K (see Fig. 2), the exothermic peak for the amorphous phase's crystallization is indistinct, indicating that the alloy is occupied by the crystalline structure dominantly.

3.2. SEM analysis

Fig. 3 shows SEM back-scattered electron (BSE) images and EDS results. Figs. 3(a)–(c) show a homogeneous microstructure for the φ3 mm alloy, a microstructure of crystalline phase(s) with the matrix for the φ5 mm alloy, and a well-crystallized microstructure containing several phases for the φ10 mm alloy, respectively. The SEM results fit well with the XRD and the thermal analysis results. As can be seen from Fig. 3(b), the crystalline particles show the same contrast in the BSE image, meaning that, in the φ5 mm alloy, these particles have a unique composition. Fig. 3(d) shows typical EDS point analyses from a particle and the amorphous matrix. It is clearly shown that Al is enriched in this primary crystalline phase with depleted Zr and Ni contents. It should be noted that a small amount of

Fig. 1. XRD spectra for as-cast Zr₅₁Cu₂₀.₇Ni₁₂Al₁₆.₃ alloys formed at different cooling rates (in different sample diameters).

Fig. 2. Continuous heating curves for as-cast Zr₅₁Cu₂₀.₇Ni₁₂Al₁₆.₃ alloys formed at different cooling rates (in different sample diameters), in which the crystallization enthalpy for the φ3 and φ5 mm Zr₅₁Cu₂₀.₇Ni₁₂Al₁₆.₃ alloys are presented.
oxygen (∼3 at%) has been detected in this crystalline phase, implying that the oxygen was involved in the formation of this phase during the solidification process.

Since there are many phases in the Φ10 mm alloy as evidenced in Fig. 3(c), an EDS line analysis was performed over several of these crystalline phases [as shown in Fig. 3(e)]. Their relevant compositions are presented in Fig. 3(f). It can be noted that Al and Zr elemental variations can be observable, suggesting that a long-range diffusion took place during the solidification process.

3.3. TEM characterization

To understand the detailed microstructures, particular to determine the crystalline phases, TEM investigation was performed on all alloys.

Fig. 4 shows a low-magnification bright-field image with an inset SAED pattern taken from the Φ3 mm alloy, confirming the amorphous nature of this alloy.

Fig. 5 shows the TEM investigation of the crystalline phase found in the Φ5 mm alloy. Fig. 5(a) is a typical bright-field image of the crystalline phase, showing the well-faceted nature of this phase. Through the series tilting technique, a series of SAED patterns titled along a dense diffraction row was obtained, as shown in Fig. 5(b). Using the projection method given by Ref. [13], a reciprocal lattice can be reconstructed as schematically shown in Fig. 5(c), in which the tilting angles between SAED patterns are given in both Figs. 5(b) and (c). Based on this analysis, the zone axes of these SAED patterns can be indexed and, from that, the structure of the primary crystalline phase can be determined to be face centered cubic (FCC) with a lattice parameter of $a = 1.21$ nm.

When the same TEM analysis is applied to the Φ10 mm alloy, the case becomes complicated. Detailed SAED and EDS analysis suggests there exist five crystalline phases in this alloy. For the convenience of discussion, these phases are denoted as $\alpha$, $\beta$, $\gamma$, $\delta$ and $\epsilon$, and Table 1 lists their averaged compositions.
Fig. 6(a) is a bright-field image taken from a typical region containing all five crystalline phases. Through reconstructing the reciprocal lattice from a series of SAED patterns for the $\alpha$ phase [as shown in Fig. 6(b)], its structure can be determined to be FCC with a lattice parameter of $a = 1.23$ nm. It is noted that the lattice parameter of this phase is slightly larger than the one found in the $F_{5m}$ alloy and is very close to the FCC NiZr$_2$ structure ($a = 1.227$ nm, space group Fd3m, a crystalline phase often found in Zr-based BMGs [14,15]). TEM EDS analysis showed 2 at% oxygen in this phase.

Fig. 6(c) is a series of SEAD patterns taken from a particle of the $\beta$ phase, which confirms that its structure also belongs to an FCC structure with a lattice parameter of $a = 0.74$ nm. This structure is close to the Al$_{1.7}$Ni$_{0.3}$Zr structure (a Cu$_3$Mg-type FCC structure, $a = 0.738$ nm). Such a crystalline phase was believed to be one of the continuous annealing products in the Zr$_{52.5}$Cu$_{27}$Ni$_8$Al$_{10}$Ti$_{2.5}$ alloy [16].

For the $\gamma$ phase, similar tilting experiment was carried out and results are shown in Fig. 6(d). Based on this, a tetragonal structure with lattice parameters of $a = 0.74$ and $c = 0.66$ nm can be determined. This structure is close to the intermetallic Zr$_3$Al$_2$ phase ($a = 0.762$ and $c = 0.699$ nm, space group P4$_2$/mmm), which was found in the Zr$_{60}$Al$_{10}$Cu$_{30}$/Co$_x$Pd$_x$ ($x = 0,10$) alloys [17].

Extensive TEM investigation suggested that the $\delta$ and $\epsilon$ phases have a rhombohedral structure and a monoclinic structure, respectively. Fig. 7(a) shows a typical bright-field image of the $\delta$ phase with an inset SAED pattern. The lattice parameters of this phase have been determined to be $a = 0.54$ nm and $c = 2.91$ nm. Fig. 7(b) shows a typical bright-field image of the $\epsilon$ phase with an inset SAED pattern. The lattice parameters of the $\epsilon$ phase are determined to be $a = 0.95$, $b = 0.55$, $c = 1.02$ nm and $\beta = 72^\circ$. Detailed determination of these two phases can be found in Ref. [18].

### 4. Discussion

Taking all the experimental results into account, following solidification sequences together with in situ formation of crystalline phases under different cooling rates (due to different diameters of rod samples) can be suggested as follows:

- For the high cooling rate (in the case of the $\Phi 3$ mm alloy), a single amorphous structure results.
When the cooling rate become moderate (in the case of the 5 mm alloy), a primary crystalline phase with an FCC structure is precipitated. For the slow cooling rate (in the case of the 10 mm alloy), significant crystallization occurs through forming multiple crystalline phases, i.e. the NiZr_2-type FCC phase, the Zr_3Al_2-type tetragonal phase, the Al_{1.7}Ni_{0.3}Zr FCC phase, a monoclinic phase and a rhombohedral phase.

As mentioned earlier, the primary crystalline phase found in the 5 mm alloy has a lattice parameter of $a = 1.21$ nm. This phase is similar to several reported crystalline phases, namely NiZr_2 ($a = 1.227$ nm) [14], Zr_3Ni_2O ($a = 1.2197$ nm) [19,20], Zr_4Cu_2O ($a = 1.227$ nm) [19] and Al_{1.7}Ni_{0.3}Zr_2 ($a = 1.208$ nm) [21]. Since oxygen has been detected in this phase, we believe that it should be the oxygen-stabilized phase—NiZr_2 or Zr_3Ni_2O [14,19,22,23]. Since this primary phase forms in the 5 mm alloy, we expect it should be the most active crystalline phase to compete with the amorphous structure. The reason of the slight difference in lattice parameters between our oxygen-stabilized phase and the standard NiZr_2 phase is possibly because a considerable amount of Cu and Al have been found in our case.

In the slow-cooled (10 mm) alloy, the lattice parameter of the NiZr_2-type phase changes from the original $a = 1.21$ nm in the 5 mm alloy to $a = 1.23$ nm. This may be due to a higher Zr content found in this alloy and Zr having the largest atomic radius among the constitutional elements ($r_{Zr} = 0.216$, $r_{Cu} = 0.157$, $r_{Ni} = 0.162$, $r_{Al} = 0.182$ and $r_{O} = 0.165$ nm). Since the NiZr_2-type phase appeared in the 5 mm alloy as the most competitive phase to the amorphous structure, it is believed that, in the slow-cooled alloy, this phase would be a leading crystalline phase. As a result of its formation, significant element diffusion takes place and results in localized composition fluctuation. This, in turn, breaks the balance of the composition for the amorphous structure and triggers the formation of other crystalline phases.

EDS linear analysis of element distribution shown in Fig. 3(f) suggests that Al and Zr are the most active elements in the slow-cooled solidification process, which in turn result in some Al-rich/Zr-poor regions or Al-poor/Zr-rich regions. Consequently, Al and Zr elements are believed to play the key role in the in situ crystallization process.

5. Conclusions

Based on the experiments and discussion outlined above, the following conclusions can be made:

(a) In the medium cooling rate (5 mm) alloy, an oxygen-containing NiZr_2-type FCC structure ($a = 1.21$ nm) has been determined to be the primary crystalline phase. In the slow-cooled (10 mm) alloy, five crystalline phases have been identified. They are the FCC NiZr_2-type phase ($a = 1.23$ nm), the FCC Al_{1.7}Ni_{0.3}Zr-type phase ($a = 0.74$ nm), the primitive tetragonal Zr_3Al_2-type phase ($a = 0.74$ and $c = 0.66$ nm), the monoclinic phase ($a = 0.95$, $b = 0.55$, $c = 1.02$ nm and $\beta = 72^\circ$) and the rhombohedral phase ($a = 0.54$ and $c = 2.91$ nm).

(b) The oxygen-stabilized NiZr_2-type crystalline phase is believed to be the most competitive phase to the amorphous structure, so that this phase acts as the leading crystalline phase to trigger the formation of other crystalline phases in the slow-cooled (10 mm) alloy.

(c) It has been observed that a long-range diffusion of Zr and Al in the slow-cooled (10 mm) alloy, which is believed to play the key role in the in situ crystallization process.

Fig. 6. (a) TEM bright-field image showing the well-crystallized microstructure in the 10 mm alloy Zr_{51}Cu_{20.7}Ni_{12}Al_{16.3}. Five crystalline phases, $\alpha$, $\beta$, $\gamma$, $\delta$ and $\varepsilon$, are specified, (b) SAED patterns for the $\alpha$ phase, (c) SAED patterns for the $\beta$ phase and (d) SAED patterns for the $\gamma$ phase.
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Fig. 7. TEM bright field images and corresponding inserted SAED patterns for: (a) the rhombohedral phase and (b) the monoclinic phase found in the $\Phi 10$ mm alloy Zr$_5$Cu$_{20.7}$Ni$_{12}$Al$_{16.3}$. 

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