Short communication

Crystallization behavior of the Zr\textsubscript{63}Al\textsubscript{7.5}Cu\textsubscript{17.5}Ni\textsubscript{10}B\textsubscript{2} amorphous alloy during isothermal annealing

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Abstract

The crystallization behavior of Zr\textsubscript{63}Al\textsubscript{7.5}Cu\textsubscript{17.5}Ni\textsubscript{10}B\textsubscript{2} amorphous Alloy was studied by means of scanning differential calorimetry (DSC), X-ray diffraction (XRD), and transmission electron microscopy (TEM). A single stage transformation of the amorphous phase forming a Zr\textsubscript{2}Cu-type crystalline phase was observed. Kinetics for such single stage crystallization was analyzed by means of Johnson–Mehl–Avrami equation and discussed regarding to the value of Avrami exponent. In addition, the cube of crystal size presents a linear relationship with isothermal annealing time. This indicates that the crystallization process of Zr\textsubscript{63}Al\textsubscript{7.5}Cu\textsubscript{17.5}Ni\textsubscript{10}B\textsubscript{2} amorphous alloy belongs to thermally activated process of Arrhenius type. From the HRTEM analysis, small amount of Zr\textsubscript{2}Cu-type crystals in the nano-scale dimension (10–20 nm) were observed to precipitate from the amorphous matrix upon the early stage of isothermal annealing the amorphous alloy at the temperature between the glass transition (\(T_g\)) and the onset crystallization temperature (\(T_x\)).

Keywords: A. Nanostructured intermetallics; B. Glasses, metallic; B. Grain growth; B. Phase transformations; B. Thermal stability

1. Introduction

In recent years, a great of attention has been devoted to the mechanism of the high stability of supercooled liquid in the bulk metallic glasses (BMGs), such as the Mg-[1,2], the La-[3], the Ti-[4], and the Zr-based-[5–7] systems. Among these metallic glasses, the Zr-based metallic glass is considered to be one of the most promising materials and has much attractive attention due to its exceptional glass-forming ability (GFA) with a critical cooling rates as low as 1 k/s and an extremely wide super cooled liquid region exceeding 100 K [6,8]. The supercooled region, \(\Delta T_x\), is defined as the difference between the glass transition temperature \(T_g\) and the onset crystallization temperature \(T_x\). Another attractive characteristic of the BMG is its unique properties, such as high corrosion resistance, excellent elastic and mechanical properties [9–11] for Zr-based amorphous alloys. In addition, the tensile fracture strength of the Zr-based amorphous alloy reaches 1600–1800 MPa at room temperature and their densities are around 5.9–6.7 Mg/m\(^3\) [12]. Therefore, the high specific strength of the BMG is expected to extend the application of bulk amorphous alloys.

Based on the fact that this series of new amorphous alloy posses a wide supercooled liquid region, the glass forming ability (GFA) of an alloy which Inoue [13] proposed to define as the critical cooling rate \(R_c\) (the minimum cooling rate to obtain a BMG) can be evaluated by both values of \(T_{rg}\) and \(\Delta T_x\), where \(T_{rg}\) is defined as \(T_g/T_m\) and \(T_m\) is the onset melting temperature. Lu and Li [14] also showed recently that the best forming composition for BMG alloys is at or the near eutectic composition, at which the reduced glass transition temperature \(T_{rg}\) given by \(T_g/T_l\) reaches the highest value, where \(T_l\) is the offset melting temperature. Since \(T_l\) plays the most influential role in glass formation, one must look for regions of exceptionally low-lying \(T_l\) in the alloy phase diagram, such as the eutectic region.

Inoue and Masumoto [13,15,16] also revealed the relationship between the thermal stability of amorphous phase and the topological short-range ordering. It is generally thought that the increase in packing density would cause an increase in thermal stability and mechanical
strength of an amorphous phase. Therefore, the low values of \( T_x \) and mechanical strength for the binary amorphous alloys are presumably because their amorphous structure has a looser atomic configuration as compared with that for the ternary and the quaternary amorphous alloys. In this study, the Zr\(_{63}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)B\(_2\) alloy with a high activation energy of crystallization (about 360 kJ/mol) [17] is selected to study the crystallization behavior during isothermal annealing process between \( T_g \) and \( T_x \).

2. Experimental procedure

The chemical composition of the alloy used in this study is based on Zr\(_{63}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)B\(_2\) by atomic percentage. The pre-alloyed ingots were prepared by arc melting of the appropriate mixture of pure elements, including Zr (99.8 wt% purity), Ni (99.9 wt% purity), Cu (99.99 wt% purity), Al (99.99 wt% purity), and B (99.99% purity), in an argon atmosphere. The alloy ribbon samples of about 0.1 mm in thickness and 5 mm in width were prepared by the single roller melt-spinning technique in an argon atmosphere. The thermal property of the as-quenched samples was characterized by TA Instruments DSC 2920 differential scanning calorimeter (DSC). All amorphous ribbons were isothermally annealed at a temperature between \( T_g \) and \( T_x \) in vacuum at different time. The as quenched and the annealed structure were examined by Scintag X-400 X-ray diffraction (XRD) with monochromatic CuZ K\(_\alpha\) radiation and transmission electron microscopy (Joel 300CX TEM) with nano beam electron diffraction.

3. Result and discussion

The kinetic study of crystallization was performed by using the Johnson–Mehl–Avrami (JMA) [18] isothermal analysis for volume fraction \( x \), which is transformed as a function of time \( t \) based on the following Eq. (1):

\[
x(t) = 1 - \exp[-(kt)^n].
\]

These samples were annealed isothermally at several temperatures between \( T_g \) and \( T_x \). The volume fraction transformed versus the annealing time plots for Zr\(_{63}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)B\(_2\) alloy is shown in Fig. 1. For each annealing temperature (\( T_a \)), the time needed to reach 30, 50, and 80% crystallinity was individually recorded to plot curves of \( \ln t \) versus \( 1/T_a \), as shown in Fig. 2(a). The activation energy was determined to be 380 kJ/mol for the Zr\(_{63}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)B\(_2\) alloy by the slope. This value is about 20% higher than the activation energy of crystallization for the Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\) alloy (314 kJ/mol). This indicates that the additions of boron can improve the thermal stability of the Zr-based alloy.

In additions, Eq. (2) can be rewritten as:

\[
\ln[\ln(1/(1 - x))] = n \ln(k) + n \ln(t).
\]

Fig. 1. Isothermal transformation curves of the Zr\(_{63}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)B\(_2\) alloy at different temperature.

Fig. 2. (a) Plots of \( \ln t \) versus \( 1/T_a \) for different fractions of crystallization to derive the activation energy for Zr\(_{63}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\)B\(_2\) alloy. (b) JMA plots constructed for 0.1\( \times \)0.9 from the isothermal transformation curves depicted in Fig. 2.
where $k$ is the effective rate constant and $n$ is the Avrami exponent. Avrami plots of $\ln[-\ln(1-x)]$ versus $\ln(t)$, constructed for 0.1 to 0.9 from the curves at different temperatures in Fig. 2(b). The average value of the Avrami exponent $n$ was 1.75 for Zr$_{63}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$B$_2$ alloy at the temperature range from 694 to 700 K, which is similar to the value (1.96 ± 0.25) of Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$ alloy. This indicates that these two alloys present similar crystallization behavior, with a decreasing nucleation rate [19].

Fig. 3 shows the XRD pattern of the as-spun Zr$_{63}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$B$_2$ alloy. A broad maximum with two small peaks of Zr$_2$Ni (211) and Zr$_2$Cu (103) was observed of this alloy in this study. In parallel, the TEM examination revealed that the structure of the as-quenched ribbon was not quite uniform. This can be illustrated by the HRTEM (high resolution TEM) as shown in Fig. 4. The majority of the matrix was amorphous phase (as shown in Fig. 4(a)) but

Fig. 3. XRD pattern of as-quenched Zr$_{63}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$B$_2$ alloy.

Fig. 4. HRTEM images of the as-quenched alloy 4Si: (a) bright field image, (b) SAD of the amorphous matrix, (c) dark field image from the (103) reflection of Zr$_2$Cu phase.

Fig. 5. HRTEM lattice image of the Zr$_{63}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$B$_2$ alloy annealed at 681 K at different time; (a) 0 s, (b) 300 s, and (c) 1000 s.
some ultra fine crystalline particles with random orientation, of size about 5 to 10 nm, were embedded in the amorphous matrix (as shown in Fig. 4 (b)). Each single particle examined by the HRTEM image is confirmed to be single crystals of tetragonal-structured Zr2Cu type crystalline phase. This is analogous to the previous reported by Massalski et al. [20] and Jang et al. [21]. Both research teams discovered that a single metastable crystalline phase with a size about 10 nm formed near the glass transition temperature during rapid solidification from the melt.

When the Zr63Al7.5Cu17.5Ni10B2 alloy annealed at 681 K for 300 s, the average size of Zr2Cu type nano-crystals grows from 5 to 12 nm, as shown in Fig. 5(a) and (b). In addition, the average size of Zr2Cu type nano-crystals increases to 20 nm with annealing time up to 1000 s, as shown in Fig. 5(c). The crystal size measured by TEM exhibits increases monotonously with increasing $t_a$ and shows a good linear relationship between the annealing time $t_a$ and the cube of particle size of the Zr2Cu type crystalline phase, as shown in Fig. 6. This can be described by the following Eq. (3):

$$D_t^3 - D_0^3 = k t_a$$

where $D_0$ is the particle size in diameter at $t_a=0$, $D_t$ is the particle size at $t_a=t$, and the rate constant $k$ depends on temperature in the Arrhenius relation. This result is analogous to the growth behavior with thermal activation process of Arrhenius type reported by Saida [22].

4. Conclusion

According to the results of DSC, X-ray diffraction, HRTEM observation, and SEM observation for the Zr63Al7.5Cu17.5Ni10B2 alloy, the crystallization behavior and mechanical properties of Zr63Al7.5Cu17.5Ni10B2 alloy can be summarized as:

(1) The activation energy of crystallization for the Zr63Al7.5Cu17.5Ni10B2 alloy was about 380 kJ/mol as determined by the Arrhenius plot. These values are 20% higher than the activation energy of crystallization for the Zr65Al7.5Cu17.5Ni10 alloy (314 kJ/mol). This indicates that the boron addition exhibits the effect on improving the thermal stability of the Zr65Al7.5Cu17.5Ni10 alloy.

(2) The average value of the Avrami exponent $n$ was calculated to be 1.75 for Zr63Al7.5Cu17.5Ni10B2, which is similar to the value (1.96) of Zr65Al7.5Cu17.5Ni10 alloy. This indicates that these two alloys present the similar crystallization process, with a decreasing nucleation rate.

(3) The changes in crystal size with increasing annealing time shows a good linear relationship between annealing time and the cube of crystal size of the Zr2Cu type crystalline phases. This indicates that the crystal growth of the alloy belongs to thermally activated process of Arrhenius type.

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References
