Arch. Metall. Mater. **62** (2017), 2B, 1023-1026

DOI: 10.1515/amm-2017-0146

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CRYSTALLIZATION BEHAVIOR OF $Zr_{62}Al_8Ni_{13}Cu_{17}$ METALLIC GLASS

The crystallization behavior has been studied in $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass alloy. The $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass crystallized through two steps. The fcc Zr_2Ni phase transformed from the amorphous matrix during first crystallization and then the Zr_2Ni and residual amorphous matrix transformed into a mixture of tetragonal Zr_2Cu and hexagonal Zr_6Al_2Ni phases. Johnson-Mehl-Avrami analysis of isothermal transformation data suggested that the formation of crystalline phase is primary crystallization by diffusion-controlled growth.

Keywords: Metallic glass, Crystallization, Kinetics, Amorphous, Zr-based

1. Introduction

In general, a metallic glass is formed by continuous cooling from the liquid state of an alloy at a rate sufficiently high to avoid its crystallization. In order to form a glass, competing crystalline phase must be avoided during solidification, while a metastable phase generally is produced during heat treatment of the glass. Upon heating, most metallic glass crystallize initially to one or several metastable phase [1,2]. In such case, the maintenance of the liquid structure during solidification, i.e. glass formation, is not related to crystallization of metastable phase but is associated with avoidance of competing crystalline phase during solidification. Therefore, consideration of crystallization behavior is of interest from the glass formation point of view.

Crystallization kinetics of the amorphous to crystallization phase during annealing has currently attracted significant interest among scientists [3,4], because of its potential to give insight about the relationship between amorphous and crystalline structure, and the growth kinetics of nanocrystal in undercooled liquid.

Since the metallic glasses crystallize by a nucleation and growth process, crystallization process offers a unique opportunity of study under controlled conditions of the growth of crystals. Also, controlled crystallization of amorphous alloys can be adapted to obtain partially crystallized materials with nanometer-sized crystallinity embedded in the residual amorphous matrix. This nanocrystal/amorphous composite structure with appropriate compositions allows the materials to exhibit excellent mechanical or magnetic properties [5,6]. It has been reported that crystallization mode is related to the appearance of a wide supercooled liquid region before crystallization [7]. Therefore, study on crystallization kinetics is essential for development of the metallic glasses and the nanocrystalline materials. The study on crystallization behavior in the supercooled liquid region of metallic glasses will help to control and optimize the properties of metallic glasses.

In this study, crystallization behavior of $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass has been studied. Also, the crystallization sequence and the kinetic behavior of crystalline phase formation from amorphous $Zr_{62}Al_{10}Ni_{11}Cu_{17}$ alloy during the annealing have been studied systematically.

2. Experimental

Alloys of $Zr_{62}Al_8Ni_{13}Cu_{17}$ was prepared by arc melting pure metals Zr (99.9%), Al (99.9%), Ni (99.9%), Cu (99.9%), under an argon atmosphere. To reduce the possibility of oxygen contamination, pure Ti known as a good getter for oxygen was melted prior to the melting of the elements. To improve the homogeneity of the alloy button, the button was re-melted three times.

$Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass ribbon was prepared by melt spinning under an Ar atmosphere. For melt spinning, the alloy was re-melted in quartz tubes, followed by ejecting with an over pressure of 35 kPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. The resulting ribbons exhibit thickness of about 50 μm and width of about 2 mm. Heat treatment of specimens was performed under an Ar atmosphere at different temperatures from 748 to 778 K in order to indentify the exothermic reaction.

A differential scanning calorimetry (DSC, Perkin Elmer, DSC8000/8500) which has a temperature scanning range from

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room temperature to 973 K, was used to identify the phase transformations such as glass transition and crystallization. The heating rates for non-isothermal scans was 40 K/min. Both non-isothermal and isothermal DSC can be used to study the phase transformation kinetics. Isothermal DSC experiments were performed at different temperature from 695 to 704 K in the supercooled liquid region.

Initial characterization and the phase transformation behavior during annealing of the sample was performed by X-ray diffraction (XRD, Rigaku, MiniFlex600) with Cu target (λ = 1.5404Å).

3. Results and discussion

The XRD pattern of $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass ribbon exhibits typical broad diffraction peak indicating an amorphous structure without distinct crystalline peaks, as shown in Fig. 1.

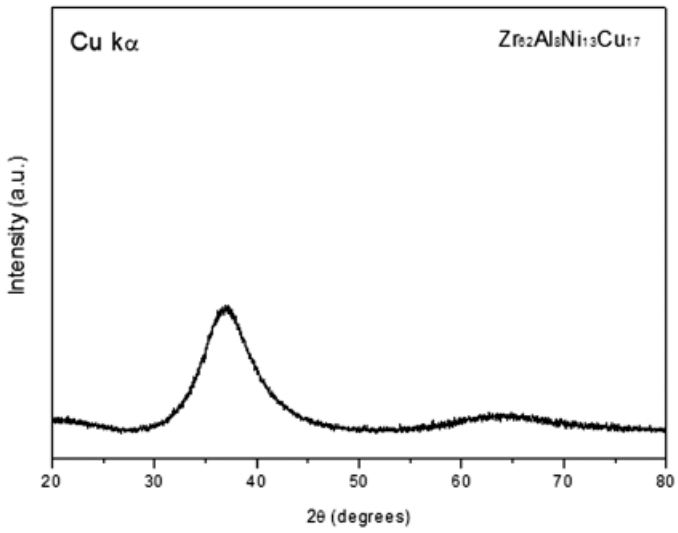


Fig. 1. XRD trace obtained from melt-spun $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass

Fig. 2 shows a typical DSC curve obtained during continuous heating at a heating rate of 40 K/min in the range of 600-850 K. The $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass ribbon shows an endothermic reaction corresponding to glass transition to supercooled liquid, and two overlapping exothermic peaks corresponding to crystallization of the supercooled liquid. The $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass ribbon shows glass transition temperature (T_g) of 680 K and onset temperature of the crystallization (T_x) of 735 K. The supercooled liquid region, defined as $\Delta T_x = T_x - T_g$ indicating the stability of supercooled liquid against crystallization, is about 55 K.

DSC curve of the melt-spun $Zr_{62}Al_8Ni_{13}Cu_{17}$ exhibits two overlapped exothermic peaks corresponding to crystallization of the supercooled liquid as shown in Fig. 2. In order to identify the crystallization products or each exothermic reaction, three heat treatments were separately performed up to the finishing temperature of exothermic reactions as shown in Fig. 3(a).

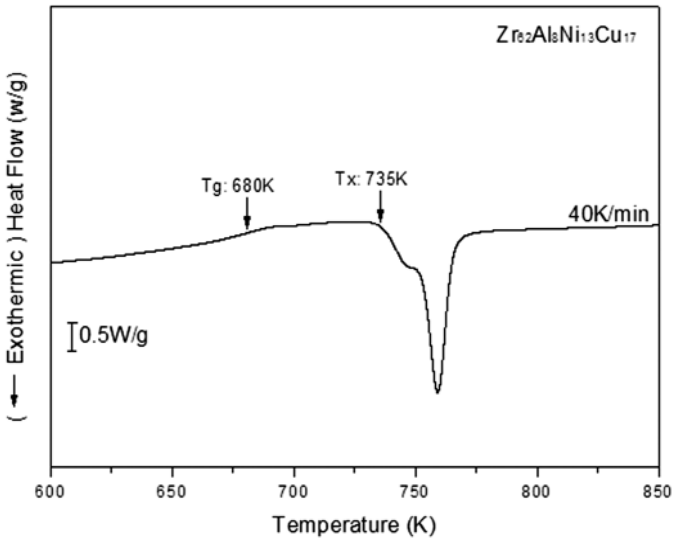
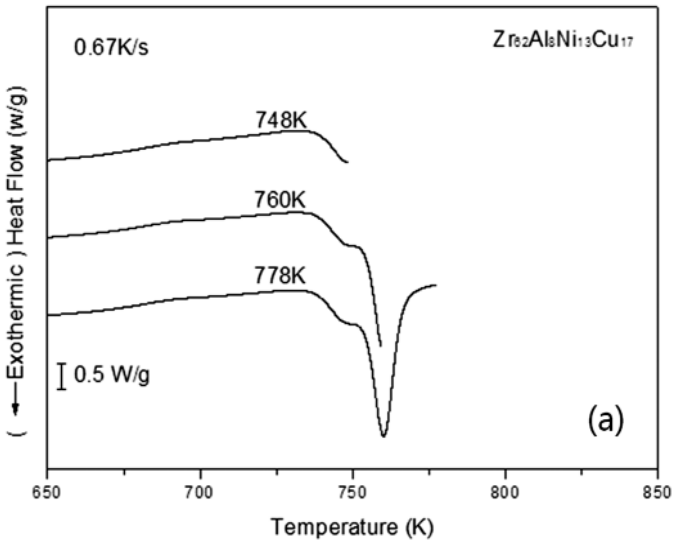


Fig. 2. DSC curve obtained from melt-spun $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass during continuous heating



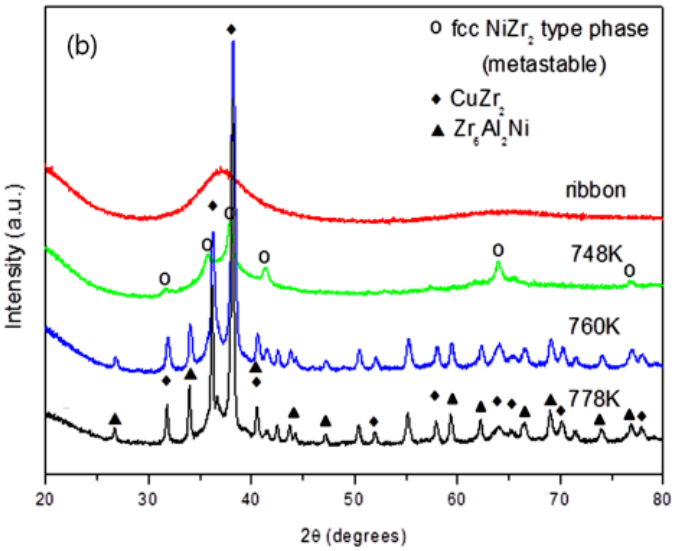


Fig. 3. (a) DSC curves and (b) XRD trace of the $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass annealed at different temperatures

Fig. 3(b) shows typical XRD traces obtained from the annealed $Zr_{62}Al_8Ni_{13}Cu_{17}$ ribbon, together with the data of melt-spun ribbon. The XRD trace from the melt-spun ribbon shows a broad halo pattern, characteristic of the amorphous structure. The sample heated to the onset temperature of the first exothermic reaction (T = 748 K), shows sharp diffraction peaks superimposed on a weak halo pattern, indicating partial crystallization occurs. The diffraction peaks are analyzed to be a metastable fcc Zr_2Ni phase. Therefore, the first crystallization exotherm of $Zr_{62}Al_8Ni_{13}Cu_{17}$ alloy corresponds to primary crystallization of amorphous phase into an fcc Zr_2Ni phase. The XRD trace taken from the partially annealed (T = 760 K) and fully annealed (T = 778K) samples for the second exothermic reaction show several sharp diffraction peaks. These peaks are analyzed to be a mixture of tetragonal Zr_2Cu and hexagonal Zr_6Al_2Ni phases precipitated simultaneously during the second crystallization reaction.

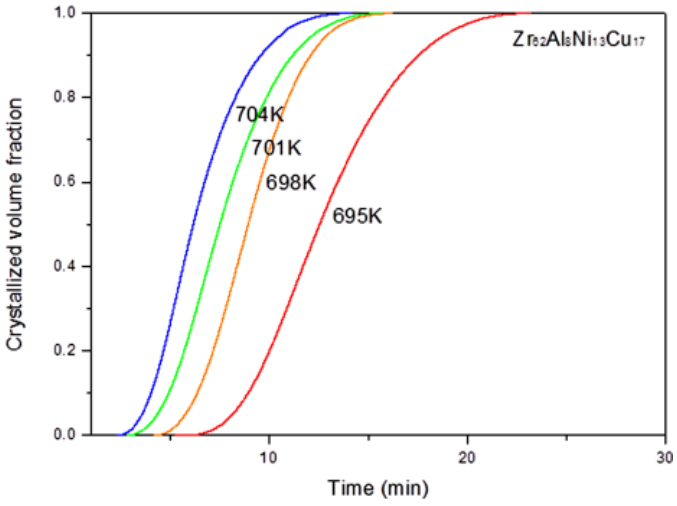


Fig. 4. Volume fraction of crystalline phase in amorphous matrix as a function of annealing time at different temperature for $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass

The kinetic behavior of the transformation from amorphous to crystalline phase was studied by isothermal DSC experiments. The isothermal DSC curves were analyzed by the Johnson-Mehl-Avrami (JMA) equation [8,9] after careful baseline correction. The fraction x of crystalline phase at time t during isothermal annealing can be expressed as follow:

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

where τ, k and n are the incubation time, rate constant and Avrami exponent, respectively. The fraction of the crystalline phase was assumed to be same as that of heat release. Fig. 4 shows typical sigmoidal-type curves of $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass ribbons at different temperatures. The slope of curve the crystallized volume fraction x versus time correspond to the crystallization rate at constant heating rate indicates that the crystallization rate of $Zr_{62}Al_{10}Ni_{11}Cu_{17}$ metallic glass ribbons is enhanced when the volume fraction x is in the range of 20~80%.

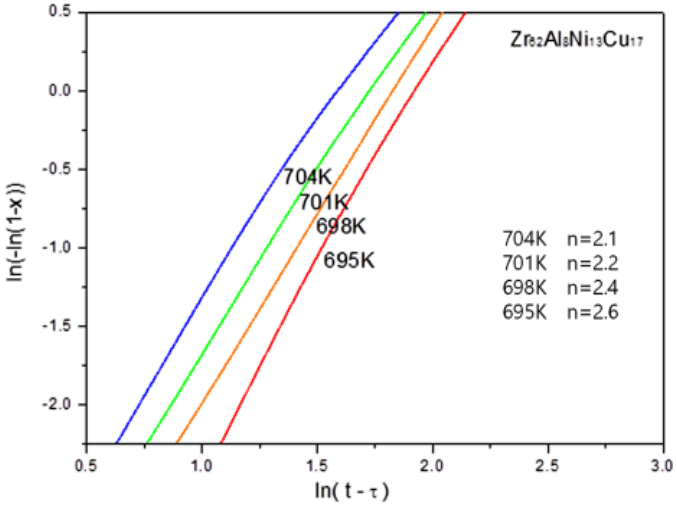


Fig. 5. Avrami plots for the exothermic peak of the $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass at different temperatures

Fig. 5 shows replots of isothermal DSC exotherms into a form of $\ln[\ln(1/1-x)]$ against $\ln(t-\tau)$. In the range from $x = 0.1$ to 0.9, the linear relationship between $\ln[\ln(1/1-x)]$ and $\ln(t-\tau)$ appeared. The Avrami exponent n was obtained from the slope of the straight line in the range from $x = 0.1$ to 0.9. The n varied from about 2.1 to 2.6. The average Avrami exponent of about 2.3 implies that crystallization mechanism of $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass is primary crystallization by diffusion-controlled growth with decreasing nucleation rate [10].

Fig. 6 shows typical bright field TEM image of $Zr_{62}Al_8Ni_{13}Cu_{17}$ alloy obtained after annealing treatment for 60 s at 778 K. The microstructure consisted of equiaxed grains with typical size of about 40 nm. From the XRD results mentioned above, the equiaxed grains can be analyzed to a mixture of tetragonal Zr_2Cu and hexagonal Zr_6Al_2Ni phases.

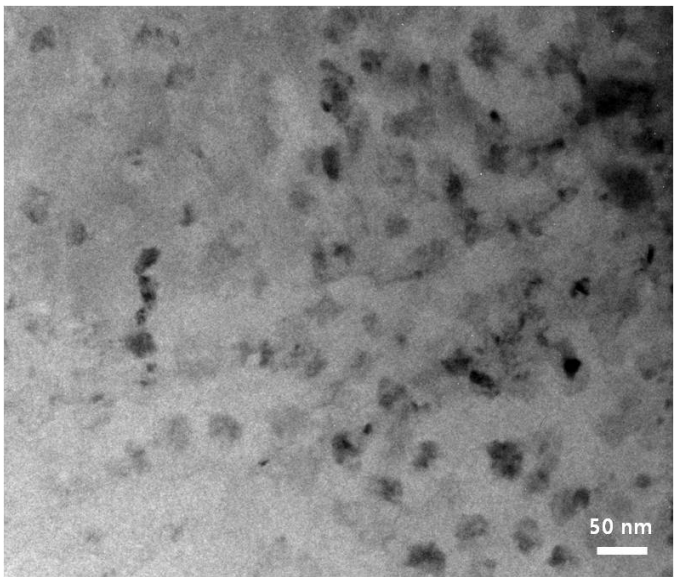


Fig. 6. Typical bright field TEM image obtained from $Zr_{62}Al_8Ni_{13}Cu_{17}$ ribbon specimen annealed for 60 s at 778 K

4. Conclusions

In this study, crystallization sequence and kinetic behavior of $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass was studied. The $Zr_{62}Al_8Ni_{13}Cu_{17}$ metallic glass crystallized through two reactions. First, primary crystallization of fcc Zr_2Ni phase nucleated from the amorphous matrix and then the fcc Zr_2Ni and remaining amorphous phase transformed into a mixture of tetragonal Zr_2Cu and hexagonal Zr_6Al_2Ni phases. In the Johnson–Mehl–Avrami analysis, the Avrami exponent is in the range from 2.1 to 2.6, indicating the transformation is close to be primary crystallization by diffusion-controlled growth.

Acknowledgments

This work was supported by the research grant of the Kongju National University in 2014.

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