

STUDY OF FORMATION OF NANO-QUASICRYSTALS AND CRYSTALLIZATION KINETICS OF Zr–Al–Ni–Cu METALLIC GLASS

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Abstract

The formation of nano-quasicrystals on isothermal annealing of melt-spun ribbons of $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$ metallic glass has been investigated using transmission electron microscopy (TEM). The crystallization study of this metallic glass has been carried out using differential scanning calorimetry (DSC) in non-isothermal (linear heating) mode. It exhibits two-stage crystallization where the first stage corresponds to the precipitation of icosahedral nano-quasicrystalline phase. This has been confirmed with the help of TEM investigations. The crystallization parameters like the activation energy (E_c) and frequency factor (k_0) have been derived using the Kissinger peak shift analysis. The activation energies for the first and second crystallization peak are found to be 278 and 295 kJ mol^{-1} , respectively. The frequency factors obtained for the two peaks are respectively $7.16 \cdot 10^{19}$ and $1.42 \cdot 10^{20} \text{ s}^{-1}$. E_c , k_0 and the Avrami exponent (n) have also been derived by fitting the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation for the transformed volume fraction (x) to the crystallization data. JMAK results of E_c for the first and second crystallization peak turn out to be 270 and 290 kJ mol^{-1} respectively. However, k_0 and n are found to be heating rate dependent as reported in similar studies. The values of n for the first crystallization stage ranges between 1.66 and 2.57 indicating diffusion-controlled transformation in agreement with earlier reports.

Keywords: crystallization kinetics, icosahedral nano quasicrystals, Zr–Al–Ni–Cu metallic glass

Introduction

Zr–Al–Ni–Cu is among the families of best glass-forming alloys. It possesses an undercooled liquid region $\sim 100 \text{ K}$ [1] and shows high thermal stability with respect to crystallization. Isothermal annealing of these alloys produces a metastable icosahedral phase increasing the stability of glassy state [2–4]. The precipitation of nano-quasicrystalline phase on crystallization of these alloys increases their mechanical strength combined with ductility [5]. Therefore, the knowledge of the crystallization behaviour is useful for the production of more stable glasses or design of definite microstructures by crystallization e.g. the formation of nanocrystalline materials.

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Various attempts have been made to understand the kinetics of crystallization of Zr–Al–Ni–Cu alloys in isothermal and linear heating conditions [6–8]. The kinetic parameters can be derived using the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation for the transformed volume (x) during the phase transformation in the isothermal conditions [9]. Though JMAK equation has been proposed for isothermal experiments, its use can also be extended to the non-isothermal (linear heating) experiments. Henderson [10, 11] has discussed the conditions under which the JMAK equation can be applicable to the linear heating experiments. This proposition has been exploited to evaluate the JMAK parameters from non-isothermal experiments for an iron based multicomponent glass [12]. Ruitenbergh *et al.* [13] have shown that, (i) the linear heating JMAK equation can be derived analytically for the same cases and under the same conditions as the isothermal JMAK equation, and (ii) within the JMAK framework; the non-isothermal method such as the Kissinger peak shift method can be used to analyze experimental data. Recently, in a non-isothermal study of crystallization of a $Zr_{55}Al_{10}Ni_5Cu_{30}$ glass, it has been demonstrated that the crystallization kinetic function can be described by the JMAK equation,

$$f(x) = (1-x)[- \ln(1-x)]^{(n-1)/n} \quad (1)$$

with $n=1.75$ [6]. This has guided us to investigate the non-isothermal crystallization of $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$ glass in the JMAK formalism. The crystallization study has been carried out using differential scanning calorimetry (DSC). Further, the formation of the nano-quasicrystals on crystallization during isothermal annealing of the present metallic glass has been investigated with the help of transmission electron microscopy (TEM).

Experimental

Ribbons of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ glass were prepared by a single roller melt-spinning technique in argon atmosphere. The amorphous nature of the specimen was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Koster *et al.* [4] have reported the temperature dependence of the nucleation frequency in present quaternary glass annealed for 30 min. They have pointed out that the nucleation frequency is maximum at 673 K. Knowing this, the as-quenched sample of the $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ glass was annealed at 673 K for 30 min. A TEM (Jeol, JEM-2000FX operated at 160 kV) was used for observing the microstructure. The specimen was thinned electrochemically at $-35^{\circ}C$ by jet polishing using an electrolyte with 20 % perchloric acid in ethanol. The linear heating experiments were carried out on the as-quenched samples at four different linear heating rates (2, 4, 8 and $16 K min^{-1}$) in a DSC (Shimadzu, Japan) from room temperature to 793 K. The experiments were done in the air atmosphere. The DSC has a minimum detection sensitivity of $10 \mu W$.

Results and discussion

The bright-field TEM image of the sample, annealed at 673 K for 30 min, is shown in Fig. 1a. Isothermal annealing by suddenly introducing the sample to the furnace at a constant temperature (673 K) for 30 min promotes nucleation and suppresses growth. This leads to the formation of quasicrystals of nanometric size ranging from 35 to ~100 nm. These nanometric scale quasicrystals, of icosahedral phase precipitated in the amorphous matrix, are evident in Fig. 1a. The micro-diffraction pattern of the annealed sample (Fig. 1b) reveals the icosahedral structure. Similar results for the formation of the icosahedral phase and nano-quasicrystals have been reported previously [2–4]. These studies reveal that the grain size of the quasicrystalline structure is dependent on the annealing time and the Al content in the glass. They have found out that the diameter d of the quasicrystal varies as square root of annealing time. Koster *et al.* have also observed that annealing $Zr_{67}Cu_{11}Ni_{10}Al_{12}$ for 30 min at 420°C leads to a nano-quasicrystalline structure with a mean quasicrystal diameter of about 30 nm or less [5]. Besides, quasicrystal diameters increase at a faster rate if the annealing is performed at a higher temperature. But, growth has been observed to start only after an incubation time.

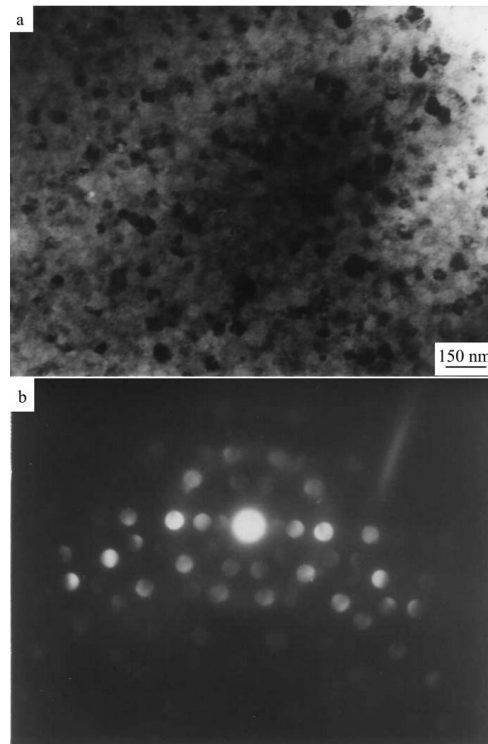


Fig. 1 a – Bright-field TEM image of a sample annealed at 673 K for 30 min;
b – Micro-diffraction pattern of a sample annealed at 673 K for 30 min

The DSC curves of as-quenched samples of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ glass at four linear heating rates are shown in Fig. 2. It exhibits a two-stage crystallization process. The first stage corresponds to the formation of the quasicrystals whereas the second stage is due to the decomposition of the quasicrystals precipitated during the first stage and the transformation of the remaining amorphous phase into crystalline phase [4]. The results are in agreement with the earlier reports [3, 4]. It can be observed from Fig. 2 that the area under the first crystallization peak, and hence the crystallization enthalpy, increases with heating rate. In fact, the signal is proportional to the scan rate. For the same heat to come out in half the time, the power has to double. Since the signal is power vs. temperature, the area under the curve doubles as the heating rate is doubled.

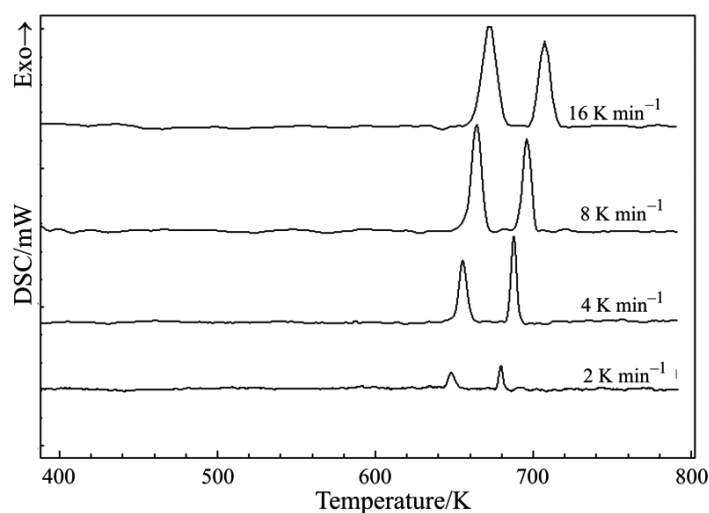


Fig. 2 DSC curves of $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$ at four linear heating rates

Further, it can be seen from the Fig. 2 that the crystallization peak shifts to the higher temperature with the increase in the linear heating rate. This indicates dynamical nature of the crystallization. The Kissinger peak shift method can be utilized to analyze the DSC data. The activation energy for crystallization (E_c) can be evaluated using the Kissinger equation [14] given by

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \ln\left(\frac{E_c}{k_B k_0}\right) + \frac{E_c}{k_B T_p} \quad (2)$$

where k_B is the Boltzmann constant, k_0 is the frequency factor, T_p is the peak temperature for crystallization and α is the linear heating rate. The plot of $\ln T_p^2/\alpha$ vs. $1/T_p$ is a straight line as shown in Figs. 3a and 3b for the first and second crystallization peaks respectively. The slope of the plot gives the activation energy (E_c) and the intercept yields the frequency factor (k_0). The so-obtained values of E_c and k_0 are given in Ta-

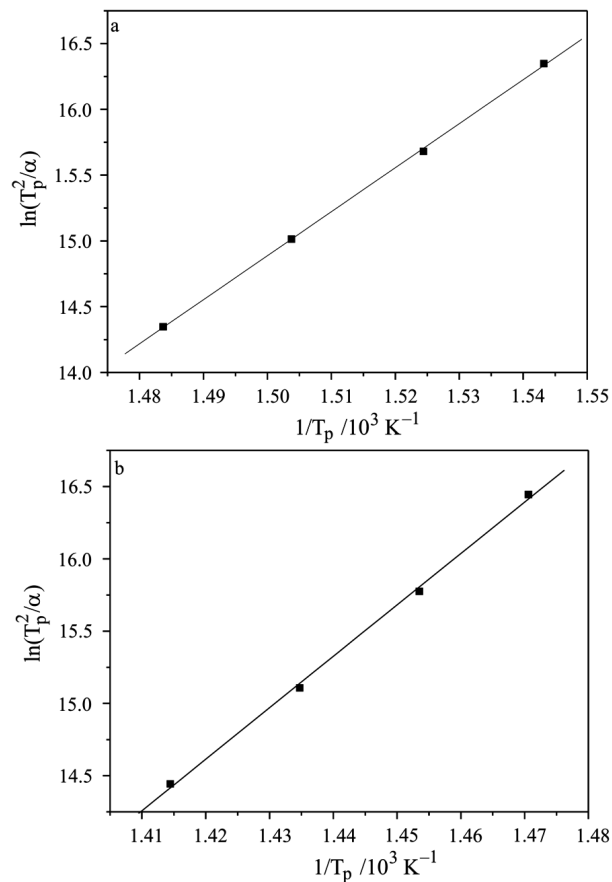


Fig. 3 a – Kissinger plot for 1st crystallization peak; b – Kissinger plot for 2nd crystallization peak

ble 1. The value of E_c equal to 278 kJ mol^{-1} for the first crystallization peak corresponding to the formation of quasicrystal formation is in close agreement with the value, 256 kJ mol^{-1} , reported for the same metallic glass [4]. The activation energy for the second crystallization is found to be 296 kJ mol^{-1} . Galwey [15] has considered the activation energy to be a physico-chemical parameter determined by the magnitude of the interatomic interactions that are activated and modified during a reaction or phase transformation. For each transformation, it should have a characteristic and constant value. Further, Kaloshkin and Tomilin [16] have given a plausible definition

Table 1 Activation energy (E_c) and frequency factor (k_0) obtained from Kissinger analysis

Crystallizaotn peak	$E_c/\text{kJ mol}^{-1}$	k_0/s^{-1}
First	278	$7.16 \cdot 10^{19}$
Second	295	$1.42 \cdot 10^{20}$

of activation energy with particular reference to crystallization of metallic glasses. The activation energy is interpreted as a threshold value which if overcome assures the start of the transformation mechanisms. The k_0 represents the atom collision probability and is usually taken as a measure of the probability that an atom having energy E_c will participate in a crystallization process [17]. The value of $k_0=7.16 \cdot 10^{19} \text{ s}^{-1}$ is of the same order of magnitude for other metallic glasses like $\text{Ti}_{45}\text{Ni}_{10}\text{Cu}_{25}\text{Sn}_5\text{Zr}_5$ ($k_0=1 \cdot 10^{20} \text{ s}^{-1}$) and $\text{Zr}_{60}\text{Cu}_{20}\text{Pd}_{10}\text{Al}_{10}$ ($k_0=1 \cdot 10^{22} \text{ s}^{-1}$) [18]. However, it is greater than the value $4.2 \cdot 10^{12} \text{ s}^{-1}$ for $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ bulk metallic glass [6]. It is because the former are the conventional melt-spun rapidly quenched metallic glasses while the later is a bulk metallic glass and the atomic mobility in bulk metallic glasses is more sluggish with respect to conventional amorphous alloys [6], leading to lower values of k_0 .

Apart from the Kissinger analysis, the experimental crystallization data can also be analyzed using the kinetic function of Eq. (1) in the JMAK framework. It is based on the isokinetic model. Recently, the isokinetic effect on the Kissinger law has been discussed [19]. The equation for the transformed volume fraction (x) can be written as,

$$x=1-\exp\left[-\frac{k_0}{\alpha}\int_{T_0}^T\exp\left(-\frac{E}{RT}\right)dT\right]^n \quad (3)$$

where T_0 is the onset crystallization temperature and n is the Avrami exponent. E_c , k_0 and n can be determined by fitting the experimental data for x to Eq. (3). The analysis of the first and second crystallization peak at four different heating rates yields E_c to be 270 and 290 kJ mol^{-1} respectively. Thus, the results are in agreement with the Kissinger analysis. The results for n and k_0 are found to be heating rate dependent and are summarized in Tables 2a and 2b for the first and second peaks respectively. The values in the tables suggest that no definite heating rate dependence of either n or k_0 could be established at this stage. However, it should be noticed that the value of n

Table 2a E_c , k_0 , n and T_p for the first crystallization peak at different heating rates

Heating rate $\alpha/\text{K min}^{-1}$	T_p/K	n	$E_c/\text{kJ mol}^{-1}$	$k_0/10^{19} \text{ s}^{-1}$
2	648	1.95	270	4.42
4	656	2.26	270	3.71
8	665	2.57	270	3.52
16	674	1.66	270	3.89

Table 2b E_c , k_0 , n and T_p for the second crystallization peak at different heating rates

Heating rate $\alpha/\text{K min}^{-1}$	T_p/K	n	$E_c/\text{kJ mol}^{-1}$	$k_0/10^{19} \text{ s}^{-1}$
2	680	1.29	280	5.11
4	688	3.31	290	1.13
8	697	2.54	290	1.36
16	707	1.78	290	1.25

ranges between 1.29 and 2.57 (except $n=3.31$ for $\alpha=4 \text{ K min}^{-1}$ for the second peak). It indicates diffusion-controlled transformation as in this case $1.5 \leq n \leq 2.5$ [20]. It is also in agreement with earlier reports by Koster *et al.* [2, 4–5].

Conclusions

TEM investigations of $\text{Zr}_{69.5}\text{Cu}_{12}\text{Ni}_{11}\text{Al}_{7.5}$ metallic glass annealed at 673 K for 30 min display the formation of nano-quasicrystals in agreement with earlier similar reports. The linear heating experiments in DSC reveal a two-stage crystallization process. The nano-quasicrystalline phase is formed during the first stage. The study of the kinetics of crystallization implies that the JMAK equation for the transformed volume fraction (x), which is originally proposed for isothermal conditions, can be utilized to analyze the data from the non-isothermal experiments as well. The Kissinger analysis yields the activation energies for the first and second crystallization peaks to be 278 and 296 kJ mol^{-1} respectively. The values of E_c from the JMAK analysis are 270 and 290 kJ mol^{-1} . The value of the Avrami exponent n ranges between 1.29 and 2.57 and indicates a diffusion-controlled transformation.

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