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Isokinetic and isoconversional study of crystallization kinetics of a Zr-based metallic glass

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ABSTRACT

The crystallization kinetics of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ metallic glass is studied under non-isothermal condition using differential scanning calorimetry (DSC). The kinetic parameters, viz. the activation energy (E) and the Avrami exponent (n), for the primary (first) crystallization peak are obtained using the isokinetic and the isoconversional methods. The so-obtained E and n are utilized to derive theoretical normalized heat flow curves through the Kolmogorov–Johnson–Mehl–Avrami (KJMA) equation. The comparison of the experimental and theoretical normalized heat flow curves at different heating rates demonstrates that the completely isokinetic description of the crystallization process is not suitable. On the other hand, the isoconversional methods in combination with the KJMA equation provide better understanding of the kinetics of the crystallization process.

1. Introduction

The kinetics of the crystallization process can be studied with the help of thermo-analytical techniques namely, differential scanning calorimetry (DSC) and differential thermal analyzer (DTA). The DSC/DTA experiments can be carried out in isothermal as well as non-isothermal (linear heating) conditions. Efforts made by the researchers in this field so far, to analyze the data obtained from DSC and hence to determine the kinetic parameters of the crystallization processes (say, activation energy, rate constant, etc.), raise two important issues: (i) the selection of the mode of experiment (isothermal or non-isothermal) and (ii) the choice of a sound method for the analysis of the experimental data. An elaborate discussion of these interlinked issues is given in Section 3. However, we are more concerned with the later issue due to the fact that several methods for the kinetic analysis are available in the literature. These methods are generally based on either the isokinetic hypothesis or the isoconversional principle and they can be accordingly categorized as (1) isokinetic methods where the transformation mechanism is assumed to be the same throughout the temperature/time range of interest and, the kinetic parameters are assumed to be constant with respect to time and temperature; (2) isoconversional methods, which are generally used for non-isothermal analysis, assume that the reaction (transformation) rate at a constant extent of conversion (degree of transformation) is only a function of temperature. The kinetic parameters, in this case, are considered to be dependent on the degree of transformation at different temperature and time. The use of isoconversional methods is widespread in the physical chemistry for the determination of the kinetics of the thermally activated solid-state reactions. The physicochemical changes during an exothermic or endothermic event in DSC (or DTA) are complex and involve multi-step (serial or parallel) processes occurring simultaneously at different rates. Therefore, the activation energies for such processes can logically not be same and it may vary with the degree of conversion. This is contrary to the isokinetic view assuming all the constituents of the material to react simultaneously at the same rate. The activation energy, in this case, is thus constant and independent of the degree of conversion. A strong difference of opinion persists among the researchers in the field of thermal analysis about the concept of variable activation energy [1,2]. In the metallurgical branch of materials science, most of the thermal phase transformations (like crystallization, recovery) are morphological and are considered to be governed by the nucleation and growth processes. The transformation mechanisms in these processes are also complex, e.g. interface-controlled, diffusion-controlled growth. Notwithstanding this, the kinetic analysis of the transformation process like crystallization is done according to isokinetic hypothesis. A few sporadic crystallization studies of metallic glasses are reported considering the variation of the kinetic parameters with the degree of conversion [3,4]. The isoconversional methods are scarcely used for the study of the crystallization kinetics of metallic glasses. In order

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to understand the relative importance of the two types of methods, a case study of the crystallization kinetics of $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$ metallic glass is taken up in the present work.

2. 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). The linear heating experiments were carried out on the as-quenched samples at four different linear heating rates (2, 4, 8 and 16 °C/min.) in a DSC (DSC-50, 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 μW. The samples of the metallic glass (3–4 mg) under consideration and the reference material α-Al_2O_3 were sealed in aluminum pans.

3. Theory

3.1. Kinetic analysis of thermally stimulated phase transformations

Most of the methods, developed to study the phase transformations involving nucleation and growth, are based on the KJMA transformation rate equation [5–7] essentially derived on the basis of experiments carried out under isothermal conditions. The KJMA rate equation is given by

$$\frac{d\alpha}{dt} = nk(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{1}$$

where α is the degree of transformation at a given time t, n is the Avrami (growth) exponent. The rate constant k is assumed to exhibit Arrhenius temperature dependence as

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where k_0 is the pre-exponential factor, E is the activation energy and R is the universal gas constant. KJMA rate equation is based on some important assumptions and it has been suggested recently that the KJMA kinetic equation is accurate for reactions with linear growth subject to several conditions and deviation from KJMA kinetics can occur if one or more of these conditions are not satisfied [8].

KJMA rate equation is often extended to non-isothermal experiments. If the transformation rate depends only on the state variables of fraction transformed, α and temperature T, and not on thermal history, then KJMA equation can be used to describe non-isothermal as well as isothermal transformation. However, Henderson [9] has argued that, in general, the transformation rate does depend on the thermal history and that Eq. (1) is valid only for non-isothermal reactions for certain special cases, namely site-saturated nucleation, a zero nucleation rate and isokinetic transformations (i.e. transformations for which $E_n = E_g$, E_n being the activation energy for nucleation and E_g for the growth), i.e. isothermal and non-isothermal transformations are governed by the same effective activation energy. The activation energy can also vary as a function of α, because a change of governing mechanism can occur upon progressing transformation. A more general modular numerical kinetic model [10,11] has been proposed that recognizes the three mechanisms, nucleation, growth, and impingement of growing new phase particles, as entities that can be modeled separately. This modular model is applicable to both isothermal and non-isothermal analyses. Even while recognizing the variation of the activation energy during the transformation, the modular model gives isokinetic description of the phase transformation. In case of complex phase transformations, the evaluation of α dependent E will be logically more useful than single activation energy. The model-free isoconversional methods are considered to be more deterministic and give trustworthy values of the α dependent E. However, activation energy only will not give a complete picture of the kinetics of phase transformation. Many times, the microstructural information (e.g. dimensionality of the growth) of the precipitating phase during the transformation is essential for understanding the kinetics of the process. Microstructure evolution during the thermally activated phase transformation process like crystallization can be described only if one take refuge to the isokinetic assumption, i.e. one assumes a particular reaction model followed by the phase transformation process. The results of the present study suggest that the complementary use of both the methods (isokinetic and isoconversional) is more useful for the understanding of the kinetics of the crystallization process.

3.2. Methods of analysis of experimental data obtained using thermo-analytical techniques

In this section, we give a brief description of some of the methods for the analysis of experimental data obtained using DSC (or DTA). We focus on the non-isothermal experiments only and the methods described are subsequently used to study the crystallization kinetics of a Zr-based metallic glass.

3.2.1. Isokinetic methods

As discussed earlier (Section 3.1), most of the isokinetic methods are based on the KJMA rate equation (Eq. (1)). For the non-isothermal experiments, $T = T_0 + \beta t$, where T_0 is the onset temperature and β is the heating rate. Then, from Eqs. (1) and (2), we can express the transformed fraction (α) as

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

There is no exact solution of the integral appearing in Eq. (3). Simplified treatment of this integral gives a linear equation [12,13] which can be used to determine E and n from the plots of $\ln[-\ln(1-\alpha)]$ vs. $1/T$ and $\ln[-\ln(1-\alpha)]$ vs. $\ln\beta$, respectively. But, this equation cannot account for the non-linearity arising in these plots and hence the evaluated E and n becomes inaccurate. Various attempts have been made to obtain accurate approximation to this integral [14,15]. Employing the approximation [14]:

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT'}\right) dT' \cong T\exp\left(-\frac{E}{RT}\right)\sum_{m=1}^{\infty}\left(\frac{RT}{E}\right)^m (-1)^{m-1} m! \tag{4}$$

and considering only $m = 1$ term, we obtain

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT'}\right) dT' \cong \frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{5}$$

Using Eq. (5) in Eq. (3), we get

$$\alpha = 1 - \exp\left[-\left\{\frac{k_0 RT^2}{\beta E}\exp\left(-\frac{E}{RT}\right)\right\}^n\right] \tag{6}$$

The values of E, n and k_0 can be determined by fitting the experimental data of α to Eq. (6) with the help of method of least squares.

Employing another approximation to the temperature integral [16]

$$\int e^{-y} y^{-2}\, dy = -e^{-y} y^{-2} \sum_{p=0}^{\infty} (-1)^p (p+1)!\, y^{-p} \tag{7}$$

where $y = E/RT$, Zhang and Mitchell [17] have obtained the following equation:

$$\ln[-\ln(1-\alpha)] = n\ln\left(\frac{Rk_0}{\beta E}\right) + n\left\{2\ln T - \frac{E}{RT} + \ln\left[1 - \frac{E}{RT} + 6\left(\frac{RT}{E}\right)^2\right]\right\} \tag{8}$$

Eq. (8) can also be used to determine E, n and k_0 using the method of least-square fitting.

3.2.2. Isoconversional methods

The isoconversional methods can be broadly classified into two categories: (1) isothermal methods and (2) non-isothermal methods. The later can further be classified as differential, integral and incremental methods. The isoconversional methods are based on the basic kinetic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{9}$$

$k(T)$ is the rate constant as given by Eq. (2) and $f(\alpha)$ is the reaction model which in case of KJMA formalism gives the Eq. (1). Eq. (9) can also be expressed in the integral form as

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha = \frac{k_0}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right) dT \tag{10}$$

As mentioned earlier, exact solution of the temperature integral is not available and various approximations made for this has resulted into different methods. A multitude of such methods is available in the literature and it is out of place to mention all of them here. We have selected a few most commonly used methods. The accuracy of various isoconversional methods and, the experimental and analytical errors associated with these methods are discussed in detail by Starink [18].

3.2.2.1. Flynn–Wall–Ozawa (FWO) method [19,20]. In this method, the temperature integral in Eq. (10) is simplified by using the Doyle's approximation [21,22] and hence we obtain:

$$\ln\beta = -1.052\frac{E}{RT} + \text{Const.} \tag{11}$$

Eq. (11) is linear and hence FWO is a linear isoconversional method. The plot of $\ln\beta$ as a function of $(1/T)$ gives the slope $(-1.052E/R)$ and subsequently one can determine the activation energy.

3.2.2.2. Kissinger–Akahira–Sunose (KAS) method [23,24]. According to the Murray and White approximation [25], the temperature integral can be approximated to be $\exp(-y^2)/y^2$, y being E/RT. Using this approximation in Eq. (10) results in the KAS equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{k_0 R}{Eg(\alpha)}\right) - \frac{E}{RT} \tag{12}$$

The slope of the plot of $\ln(\beta/T^2)$ vs. $1/T$ leads to the value of the activation energy. Based on a linear equation, KAS is also a linear isoconversional method.

3.2.2.3. Friedman method [26]. The method suggested by Friedman, utilizes the differential of the transformed fraction and hence it is called differential isoconversional method. According to this method, substituting $k(T)$ (Eq. (2)) in Eq. (9) and taking logarithm, we obtain:

$$\ln\frac{d\alpha}{dt} \equiv \ln\beta\frac{d\alpha}{dT} = \ln k_0 f(\alpha) - \frac{E}{RT} \tag{13}$$

The activation energy can be easily determined from the slope of the plot of $\ln(d\alpha/dt)$ (or $\ln(\beta d\alpha/dT)$) vs. $(1/T)$. Since this method does not take any mathematical approximation for the temperature integral, it is considered to give accurate estimate of E. However, being a differential method, its accuracy is limited by the signal noise.

3.2.2.4. Li-Tang method [27]. This method also does not make any assumption about the kinetic model and involves no approximation to the temperature integral. It is based on the following equation:

$$\int_0^\alpha \ln\left(\frac{d\alpha}{dt}\right) d\alpha = G(\alpha) - \frac{E}{R}\int_0^\alpha \left(\frac{1}{T}\right) d\alpha \tag{14}$$

where $G(\alpha) \equiv \alpha\ln A + \int_0^\alpha \ln f(\alpha) d\alpha$

3.2.2.5. Non-linear isoconversional method. For non-isothermal experiments, a non-linear method developed by Vyazovkin [28], avoids inaccuracies associated with analytical approximations of the temperature integral. For a set of m experiments carried out at different heating rates, the activation energy can be determined at any particular value of α by finding the value of $E(\alpha)$ for which the function:

$$\sum_{i\neq j}^{m}\sum^{m}\frac{[I(E_\alpha, T_{\alpha i})\beta_j]}{[I(E_\alpha, T_{\alpha j})\beta_i]} \tag{15}$$

is a minimum. The minimization procedure can be repeated for each value of α and hence the dependence of E on α can be studied.

4. Results and discussion

The DSC thermograms 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. 1. It exhibits a two-stage crystallization process. The first stage corresponds to the formation of the quasi-crystals as a result of primary crystallization whereas the second stage is due to the decomposition of the quasi-crystals precipitated during the first stage and the transformation of the remaining amorphous phase into crystalline phase [29]. The results are in agreement with the earlier reports [29,30]. In the present study, we have focused on the analysis of the first peak only.

The fractional crystallization data obtained at different heating rates have been fitted to Eqs. (6) and (8) using the iterative least-square fitting method (Fig. 2). The initial estimates for E and k_0 are obtained from the Kissinger analysis [23] and are equal to

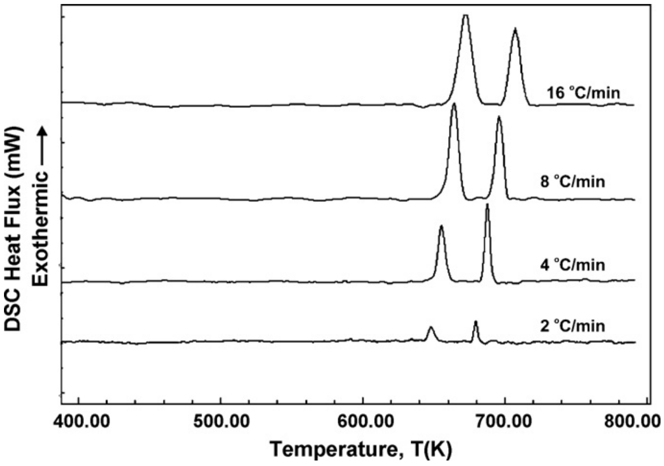

Fig. 1. DSC thermograms of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ at different heating rates.

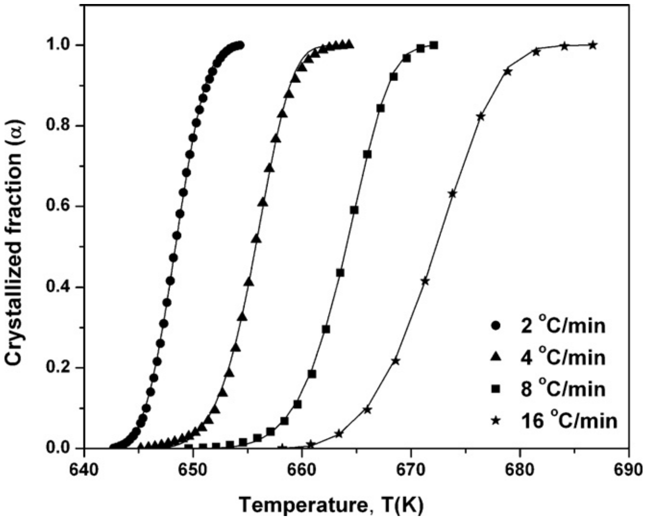

Fig. 2. Fractional crystallization data for first peak obtained from DSC thermograms. The solid line shows the least-curve fitted curve using Eqs. (6) and (8).

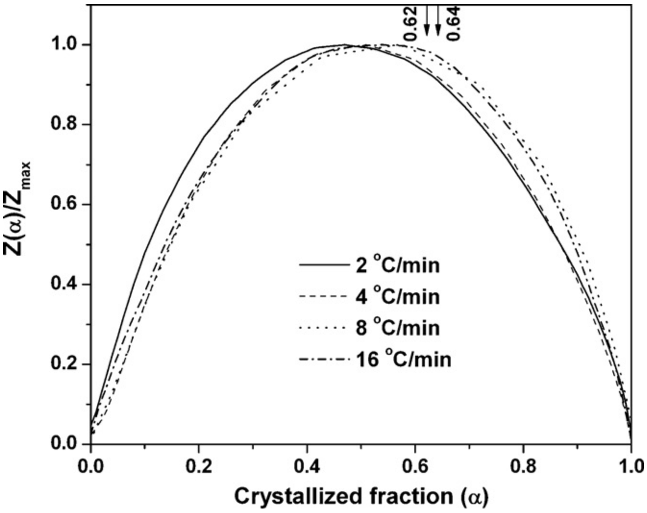

Fig. 3. The normalized function $z(\alpha)$ for different heating rates. The arrows points to the range of α where the peak of $z(\alpha)$ should fall.

278 kJ/mol and $7.16 \times 10^{19}\ \mathrm{s}^{-1}$, respectively [31]. The values of the three unknown parameters E, k_0 and n obtained from the least-square fitting are given in Table 1. It can be observed that the Avrami exponent (n) does not vary significantly and is nearly equal to 3. In case of non-isothermal experiments, it has been found that n strongly depends on the heating rate. Only if extreme cases of nucleation occur, pure continuous nucleation or pure site saturation, the value of n is independent of the heating rate and is constant ($n = 4$ or 3) [11]. It would also be observed from the results of isoconversional analysis (FWO and KAS) that α dependent n turns out to be nearly equal to 4 for the heating rates 4, 8 and 16 °C/min. It is therefore, evident that the primary crystallization is an interface-controlled process with decreasing nucleation rate [32]. In case of site saturation, the entire nucleation process takes place during early stages of the transformation and becomes negligible afterwards and the crystallization is an isokinetic process [33]. KJMA analysis using Eqs. (6) and (8) gives the overall activation energy for the first crystallization stage to be ~252 kJ/mol.

The KJMA analysis given above is based on isokinetic approximation under isothermal conditions. In order to check the applicability of the KJMA equation in non-isothermal conditions, different premonitory tests have been suggested by Henderson [9] and Malek [34,35]. Deviations from KJMA kinetics usually involve a reduced reaction rate in the later stages of the transformation, which is often detected as a deviation from the straight line expected in the plot of $\ln[-\ln(1-\alpha)]$ vs. $1/T$. Linearity of this graph was the most popular testing method for the validity of KJMA kinetics. However, it has been proved to be unreliable. A simple and practical test has been given by Malek [35]. According to this test, a function $z(\alpha) = (\mathrm{d}\alpha/\mathrm{d}T)T^2$ is plotted as a function of α. It has been suggested that the maximum of $z(\alpha)$ function should be confined to the interval $0.62 < \alpha_\mathrm{p} < 0.64$ in case of KJMA model. The present analysis shows that the peaks of the plots of $z(\alpha)$ vs. α at different heating rates lie within $\alpha_\mathrm{p} = 0.50$–0.57 (Fig. 3). Thus, α_p does not fall in the proposed interval and hence indicates deviation from KJMA model. However, it has been stated by Henderson [9] (and also remarked by Malek [35]), "a more rigorous check of the validity would of course be the direct calculation of the JMA transformation rate equation using experimentally determined kinetic parameters and a subsequent direct comparison with experimental trace". In order to check the match between the experimental and the theoretically derived normalized heat flow curves, we derive the theoretical normalized heat flow curve utilizing the calculated kinetic parameters (E and n) and the following equations:

$$\phi = \Delta H_\mathrm{c}\, k(T) f(\alpha) \tag{16}$$

with

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{17}$$

ϕ is the DSC heat flow, ΔH_c is the enthalpy difference associated with the crystallization process. Fig. 4(a)–(d) shows the comparison of the experimental normalized heat flow curves with the normalized heat flow curves derived using Eqs. (16) and (17) at different heating rates. The values of the kinetic parameters (mainly E and n) that are utilized for the derivation of the normalized heat flow curves are given in Table 1. It can be observed from Fig. 4(a) to (d) that the isokinetic results (dashed lines) (i) deviate from experimental curves in the initial stage of the crystallization and; (ii) show close match with the experimental curves starting from region near to the crystallization peak. These imply that the crystallization process involves simultaneous nucleation and growth during the initial stage, while from the region nearer to the crystallization peak the process is mainly dominated by growth, i.e. nucleation, if at all exists, becomes negligible from the region nearer to the crystallization peak and the process becomes isokinetic. This is also consistent with our foregoing observation that the primary crystallization event of the present metallic glass is an interface-controlled process with decreasing nucleation rate. Thus, it is evident that the transformation process is complex (and not isokinetic) during the entire crystallization event. The complexity of the transformation mechanism during the crystallization can be judged from the dependence of E on α. The so-called model-free isoconversional methods (Section 3.2.2) have been utilized to determine $E(\alpha)$ at different values

Table 1

Values of the Avrami (growth) exponent (n), pre-exponential factor (k_0) and activation energy (E) obtained by least-square fitting of the fractional crystallization data for the first peak at different heating rates

Heating rate (°C/min)	JMAK (Eq. (6))			Zhang and Mitchell [17] (Eq. (8))		
	n	k_0 ($10^{18}\ \mathrm{s}^{-1}$)	E (kJ/mol)	n	K_0 ($10^{18}\ \mathrm{s}^{-1}$)	E (kJ/mol)
2	2.40	1.00	250.78	2.40	1.00	250.78
4	3.08	1.00	252.19	3.07	1.53	254.78
8	3.08	1.00	252.70	3.09	1.00	252.70
16	2.21	1.37	253.95	2.22	1.10	252.73

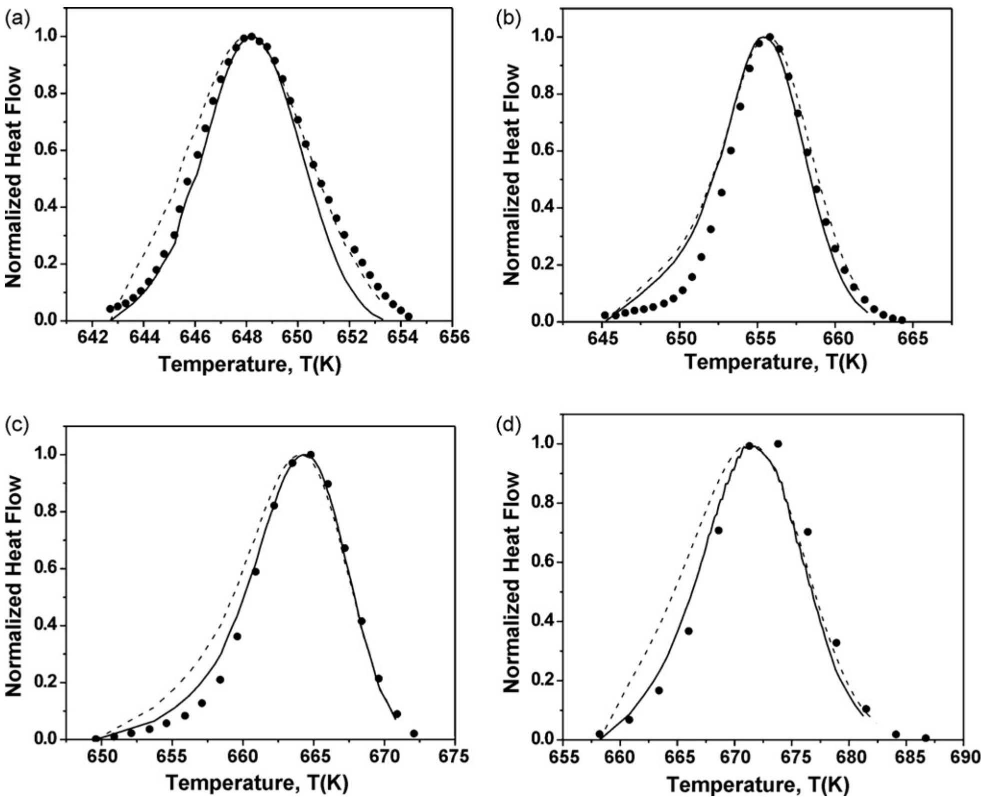

Fig. 4. Normalized heat flow curves at different heating rates (a) 2 °C/min, (b) 4 °C/min, (c) 8 °C/min, (d) 16 °C/min. (• • •), Experimental; (- - -), isokinetic results; (—), isoconversional results.

of α. The dependence of E on α is shown in Fig. 5. As can be seen from Fig. 2, the reaction is not in accordance with Eq. (9): $f(\alpha)$ is dependent on heating rate. Thus, FWO and KAS methods are not valid, and application to the data results in $E(\alpha)$ that varies appreciably with α. The Friedman [26], Li-Tang [27] and Vyazovkin [28] methods, on the other hand, show very small variation in the value of E over almost entire range of α except near the lower and higher values of α. It has been pointed out by Malek [35] that $E(\alpha)$ should be practically independent of the fractional conversion in the $0.3 \leq \alpha \leq 0.7$ range. Some changes may be expected for lower and higher values of α – particularly for fast processes – because of higher errors in the baseline interpolation for the peak tails. A pronounced variation in $E(\alpha)$ with α indicates a more complex mechanism of the crystallization process. Thus, isoconversional methods not only provide accurate value of activation energy but, it also hint towards the degree of complexity of the transformation mechanism from the knowledge of the dependence of E on α. The shape of dependence of E on α may also shed light on the kinetic scheme of the process [36]. The observed decreasing dependencies of E on α (Fig. 5) are actually the direct result of the two-exponential form of the temperature dependence of the nucleation rate, given by the Turnbull–Fisher equation [37,38]:

$$r = r_0 \exp\left(-\frac{E_D}{k_B T}\right) \exp\left(-\frac{\Delta F^*}{k_B T}\right) \tag{18}$$

where r is the nucleation rate, r_0 is the pre-exponential factor, k_B is the Boltzmann constant, E_D is the activation energy for diffusion across the phase boundary and ΔF^* is the maximum energy for nucleus formation. This equation is basically proposed for the nucleation processes that do not require long-range diffusion. However, long-range diffusion can be expected in phase transformation that involve more than one component since the new phase and the old are generally of different composition [37]. According to the classical nucleation theory, ΔF^* can be written as [32]:

$$\Delta F^* = \frac{16\pi\sigma^3 V^2}{3(\Delta G)^2} \tag{19}$$

where σ is the crystal–liquid (amorphous) interfacial energy per unit area, V is the molar volume and ΔG is the molar Gibbs free energy difference between the liquid (amorphous) and crystal phases. To estimate the value of ΔF^*, one needs to know the values of σ and ΔG as well as their temperature dependences. The interfacial energy is directly related to the entropy of fusion. Since all metals and alloys show heats of fusions that are not far away from

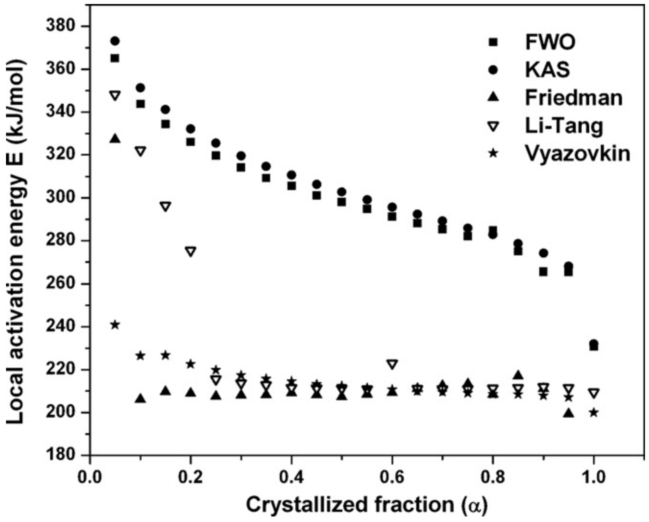

Fig. 5. Dependence of E on α obtained using different isoconversional methods.

$\Delta S \approx 8.3$ J/g atom K, the interfacial energies in supercooled liquids for moderate undercooling (far about the isentropic temperature) are always of the order of 10^{-1} J/m^2 [39]. Due to the metastable nature of the glassy state, the specific heat cannot be determined in the undercooled region. Therefore, the temperature dependence of ΔG can be obtained from one of the various approximate expressions [40,41]. The expression proposed by Thompson and Spaepen (TS) [40] has been utilized for the studies of the crystallization kinetics of Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ and Fe$_{80}$B$_{20}$ metallic glasses under non-isothermal conditions [42]. The TS expression for ΔG is given by

$$\Delta G = \frac{2\Delta H_{\mathrm{m}} T(T_{\mathrm{m}} - T)}{T_{\mathrm{m}}(T_{\mathrm{m}} + T)} \tag{20}$$

where ΔH_{m} is the molar heat of fusion and T_{m} is the melting temperature. Using Eq. (20) in Eq. (19) we get

$$\frac{\Delta F^*}{k_{\mathrm{B}}T} = \frac{\varepsilon T_{\mathrm{m}}^3 (T_{\mathrm{m}} + T)^2}{T^3 (T_{\mathrm{m}} - T)^2} \tag{21}$$

with $\varepsilon = 4\pi V^2 \sigma^3 / 3k_{\mathrm{B}} T_{\mathrm{m}} (\Delta H_{\mathrm{m}})^2$.

Since T_{m} and ΔH_{m} of the present metallic glass is not available to the best of our knowledge, we have considered an approximate melting temperature ($T_{\mathrm{m}} = 1107$ K) and the heat of fusion ($\Delta H_{\mathrm{m}} = 7245$ J/mol) of the metallic glass of slightly different composition Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$ [43]. The molar volume for this system has been calculated to be equal to 13.22×10^{-6} m^3/mol. Utilizing these values, the temperature independent parameter ε is found to be nearly equal to 1. Then, the temperature dependence of the two exponential terms in Eq. (18), $\exp(-\Delta F^*/k_{\mathrm{B}}T)$ and $\exp(-E_{\mathrm{D}}/k_{\mathrm{B}}T)$, can be illustrated as shown in Fig. 6. E_{D} is considered to be constant and it is of the order of 10^5 J/mol. The term, $\exp(-(E_{\mathrm{D}} + \Delta F^*)/k_{\mathrm{B}}T)$, representing the steady-state nucleation rate becomes maximum at 620 K, much before the onset (~640 K) of the crystallization peak in DSC. The nucleation rate then decreases in the entire temperature range of interest, 640–680 K (Fig. 6). It has already been pointed out in the earlier discussion that the first crystallization is an interface-controlled process with decreasing nucleation rate. It has also been noted from Fig. 4 that the isokinetic description of the crystallization process in JMAK formalism in terms of the normalized heat flow curve agrees well with the experimental results from the crystallization peak. That is, nucleation becomes negligible from the peak crystallization temperature (T_{p}) and the process is now mainly governed by the growth of the previously nucleated crystals.

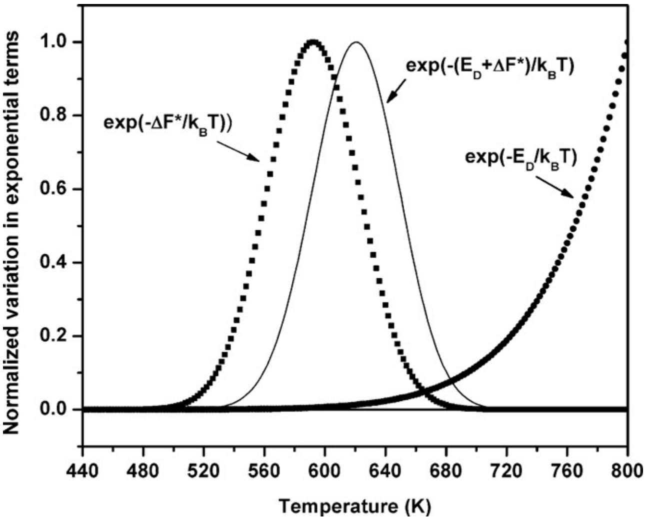

Fig. 6. Normalized variation of the exponential terms in Eq. (18) with temperature.

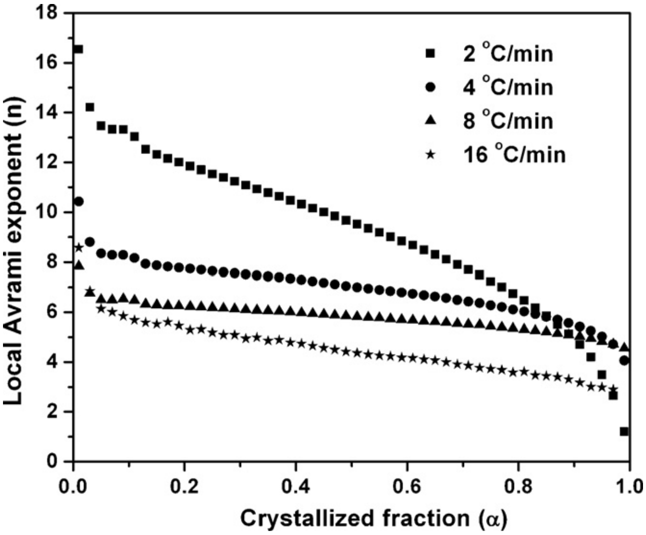

Fig. 7. Local Avrami exponent (n) derived using α dependent E.

To derive the normalized heat flow curves utilizing the α dependent values of E, we need to calculate the values of local Avrami exponent (α dependent n). The local Avrami exponent can be calculated from the following equation [44]:

$$n(\alpha) = -\frac{R}{E(\alpha)} \frac{\partial \ln[-\ln(1-\alpha)]}{\partial(1/T)} \tag{22}$$

The calculated values of the local Avrami exponent $n(\alpha)$ for different heating rates are plotted as a function α as shown in Fig. 7. The Avrami exponent n shows strong dependence on α for the heating rate 2 °C/min. whereas the variation of n is very little in the range of $0.2 < \alpha < 0.9$ for the heating rates 4, 8 and 16 °C/min. Using in Eq. (22) the $E(\alpha)$ obtained from the KAS analysis (which is more accurate than the FWO method [45,46]), the local Avrami exponent for the more reliable higher heating rates of 4, 8 and 16 °C/min is about 4. This is consistent with a reaction dominated by continuous nucleation and interface controlled growth [47]. The calculated values of $E(\alpha)$ and $n(\alpha)$ are utilized to obtain the normalized heat flow curves for different heating rates are obtained using Eqs. (16) and (17). The solid lines in Fig. 4(a)–(d) show the normalized heat flow curves where α dependent values of E obtained by isoconversional methods are used. It can be observed that the isoconversional results, in general, are very close to the experimental normalized heat flow curves. Though the present approach to derive the normalized heat flow curve does not provide any exact understanding of the mechanism involved in the reaction at hand, it does hint that complex phase transformations can be dealt with help of α dependent E and n.

5. Conclusions

The study of the primary crystallization peak of Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ metallic glass under non-isothermal heating conditions suggests that the process of phase transformation is not isokinetic during the entire temperature range (especially in the initial stage of the crystallization) of the peak. Therefore, the isokinetic description of the primary crystallization through KJMA equation using the single activation energy and the single Avrami exponent is not valid in the entire temperature range of interest. However, the use of the local activation energy and the local Avrami exponent derived using the isoconversional methods in the KJMA equation gives a better description of the primary crystallization of the metallic glass under consideration. Thus, the isokinetic methods in combination with the isoconversional methods would provide a better understanding of the kinetics of the crystallization process of metallic glasses.

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