

# Kinetics of crystallization of $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$ metallic glass

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**Abstract** Metallic glasses have received considerable attention in comparison to normal metallic materials due to their superior physical and mechanical properties. These systems possess large under cooled region,  $\Delta T$  ( $\Delta T = T_x - T_g$  where,  $T_x$  is crystallization temperature and  $T_g$  is glass transition temperature) and hence increased thermal stability against crystallization. Due to this, the study of their crystallization kinetics is important and interesting. It is interesting because of the fact that, crystallization becomes multi-step process due to several components present in these systems. In this paper, we report the experimental investigations of crystallization of  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  glassy alloy system, which is among the best non-beryllium containing glasses, using differential scanning calorimetry (DSC). The crystallization, as expected, consists of multiple steps. Interestingly, the peak heights of these steps vary with heating rate. At lower heating rates, first peak is most prominent and subsequently diminishes with increase in heating rate with last peak prominence visible at highest heating rate. Both, iso-kinetic and iso-conversional methods of analysis of kinetics of crystallization have been used to evaluate the activation energy and Avrami exponents and consistent results are obtained.

**Keywords** Crystallization kinetics · Isoconversional · Isokinetic · Metallic glass · Activation energy

## Introduction

Metallic glasses are presently among the most actively studied metallic materials. A large number of multi-component systems with excellent glass forming ability (GFA), e.g., Pd- and Zr-based metallic glasses with critical diameters larger than 1 cm have been developed. In this work, the kinetics of the crystallization of  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  glass forming alloy have been studied, which is among the best nonberyllium containing glasses, making them easier to process and to handle [1]. The crystallization kinetics can be studied with the help of thermo-analytical techniques, e.g., differential scanning calorimetry (DSC) and differential thermal analyzer (DTA). These DSC/DTA experiments can be carried out in isothermal as well as non-isothermal [2–6] environment. To analyze the data obtained from DSC and hence to obtain kinetic parameters of the crystallization processes (such as activation energy, rate constant, etc.), there are several methods available in literature. These methods are generally based on either the isokinetic hypothesis or the isoconversional principle and they can be accordingly classified as (1) isokinetic methods where rate of reaction is considered to be the same throughout the temperature/time range; and (2) isoconversional methods, which are generally used for non-isothermal (linear heating) analysis, assume that the reaction rate at a constant degree of transformation is only a function of temperature. Therefore, in the isokinetic analysis, the kinetic parameters are assumed to be constant with respect to time and temperature; while in case of isoconversional study, the kinetic parameters are considered to be

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dependent on the degree of transformation at different temperature and time [7].

## Experimental methods

Specimens of amorphous  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  alloy were prepared by a melt spinning technique. The linear heating experiments were carried out on the as-quenched samples at four different linear heating rates (5, 10, 15, and 20 °C/min) in a DSC (DSC-50, Shimadzu, Japan) from room temperature to 833 K in air. The DSC has a minimum detection sensitivity of 10  $\mu$ W. The samples of the metallic glass (5–6 mg) under consideration and the reference material  $\alpha$ - $Al_2O_3$  were crimped in aluminum pans.

## Theory

To study the phase transformation, which involves nucleation and growth, many methods are developed. Most of the methods depend on the transformation rate equation given by Kolmogorov, Johnson, Mehl, and Avrami [8–12], popularly known as KJMA equation, basically derived from experiments carried out under isothermal conditions. The KJMA rate equation is given by

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

where,  $\alpha$  is degree of transformation at a given time  $t$ ,  $n$  Avrami (growth) exponent,  $k$  the rate constant.

The Arrhenius form of the rate constant is given by

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

where,  $k_0$  is pre-exponential factor,  $E$  activation energy, and  $R$  universal gas constant.

KJMA rate equation is based on some important assumptions and it has been suggested that the KJMA kinetic equation is accurate for reactions with linear growth subject to several conditions [13].

The isoconversional methods are also known as model-free methods. Therefore, the kinetic analysis using these methods is more deterministic and gives reliable values of activation energy  $E$ , which depend on degree of transformation,  $\alpha$ . However, only activation energy will not give a perfect picture of crystallization kinetics. The microstructural information (e.g., dimensionality of the growth) of the precipitating phase during the transformation is also very important for understanding the whole kinetics of crystallization. Microstructural information would be known to us when we take the isokinetic methods into account. Therefore, the complementary use of both the methods is more useful for understanding the kinetics of crystallization.

## Results and discussion

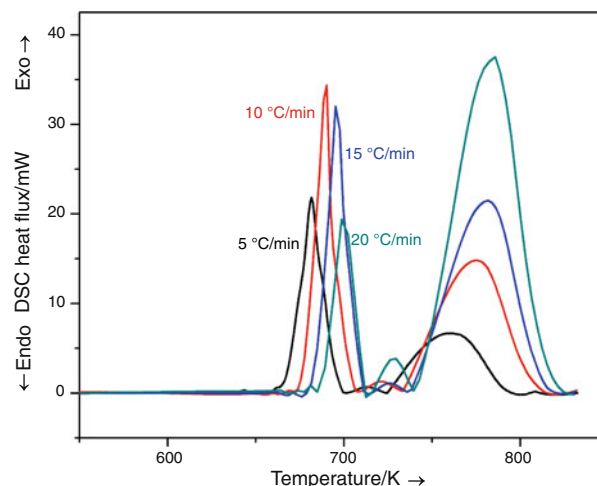
The DSC thermograms at four different heating rates (5, 10, 15, 20 deg/min) are shown in Fig. 1. The thermograms show three-stage crystallization process. The peak height of these steps varies with the heating rate. At lower heating rates, first peak is much distinct and diminishes as we go for higher heating rates and last peak visibility increases with increasing heating rate. Second peak is not much prominent in the 5, 10, and 15 deg/min heating rates. In this paper, the first peak is taken into consideration for the kinetic analysis. Glass transition temperature is not very evident in all four thermograms. The analysis of DSC data to evaluate the kinetic parameters can be obtained from non-isothermal rate laws by both isokinetic also known as model fitting methods and isoconversional methods.

### Isoconversional analysis

Isoconversional methods evaluate the activation energy values at progressive degrees of conversion  $E_\alpha$  without modelistic assumptions. The isoconversional methods can be broadly classified into two categories: (1) isothermal methods and (2) non-isothermal methods. The latter can further be classified as differential and integral methods. The isoconversional methods are based on the basic kinetic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

$k(T)$  is the rate constant as given by Eq. 2 and  $f(\alpha)$  is the reaction model which in case of KJMA formalism gives Eq. 1. The integral form of the above Eq. 3 can be given by



**Fig. 1** DSC thermograms of the metallic glass  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  at different heating rates

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

As mentioned earlier, exact solution of the temperature integral is not available and various approximations made for this has resulted into different methods. We have discussed a few most commonly used methods and kinetic parameters are calculated with the help of them. Different isoconversional methods are analyzed and discussed in detail by Starink [14].

#### Linear integral isoconversional methods

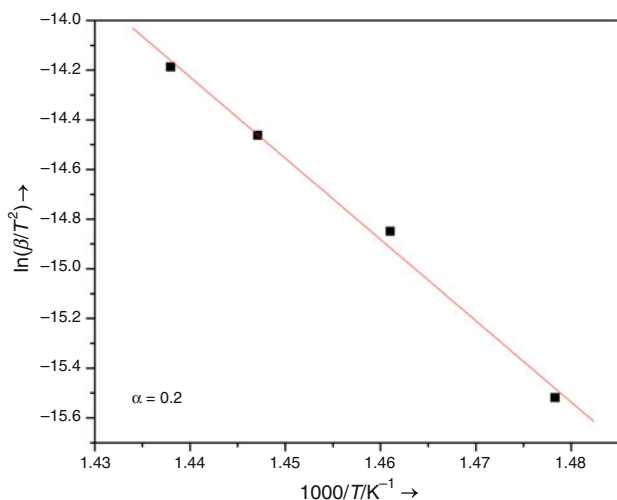
**Kissinger–Akahira–Sunose (KAS) method** Kissinger, Akahira, and Sunose [15, 16] used the approximation given by Coats and Redfern [17] to evaluate the integral in the rate Eq. 4. KAS method is based on the expression

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{k_0 R}{E g(\alpha)}\right) - \frac{E}{RT} \quad (5)$$

The activation energy can be evaluated from the slope of plot  $\ln(\beta/T^2)$  vs.  $1000/T$  for constant conversion,  $\alpha$  (Fig. 2) Values of  $E$  are given in Table 1. The discussion given ahead describes some of the methods available in the literature which are basically special cases of the KAS Eq. 5.

(i) **Kissinger method:** This well-known method assumes that the reaction rate is maximum at the peak temperature ( $T_p$ ). This assumption also implies a constant degree of conversion ( $\alpha$ ) at  $T_p$ . The equation used by Kissinger is

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left(\frac{k_0 R}{E}\right) \quad (6)$$



**Fig. 2** KAS plot at  $\alpha = 0.2$

**Table 1** Local activation energy ( $E$ ) at different conversion for different methods

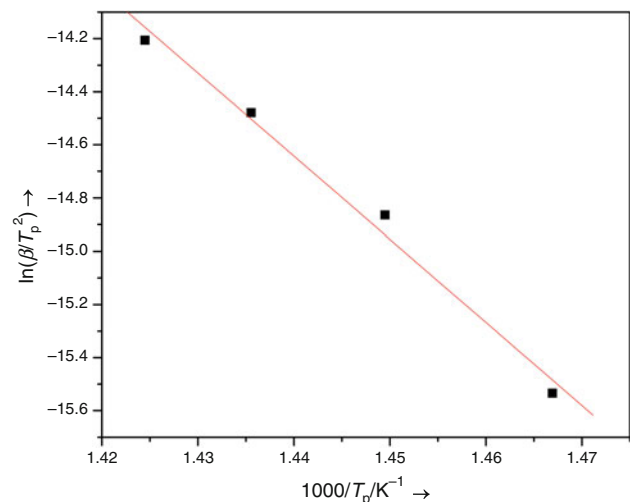
$\alpha$	$E/\text{kJ mol}^{-1}$		
	KAS	OFW	Friedman
0.1	264 ± 2	256.4 ± 2	245.5 ± 9
0.2	272 ± 2	269.5 ± 2	317.3 ± 7
0.3	278.8 ± 2	276 ± 2	303.9 ± 7
0.4	279.1 ± 2	276.3 ± 2	298.2 ± 3
0.5	280.7 ± 2	277.9 ± 2	295.7 ± 5
0.6	282.7 ± 3	279.7 ± 3	324 ± 5
0.7	285.7 ± 3	282.6 ± 3	320.7 ± 4
0.8	294 ± 3	290.5 ± 3	371.1 ± 4
0.9	303.8 ± 2	299.9 ± 2	360.5 ± 2

A plot of  $\ln(\beta/T_p^2)$  vs.  $1000/T_p$  (Fig. 3) gives an approximate straight line and the activation energy  $E$  and pre-exponential factor  $k_0$  is calculated using the slope and the intercept (Table 2).

(ii) **Augis and Bennett's method:** This method was suggested by Augis and Bennett [18] and is an extension of Kissinger method showing its applicability to heterogeneous reaction described by Avrami expression. Apart from the peak crystallization temperature it also incorporates the onset temperature of crystallization,  $T_o$  and it is supposed to be a very accurate method of determining  $E$  through the equation

$$\ln\left(\frac{\beta}{(T_p - T_o)}\right) = -\frac{E}{RT_p} + \ln k_0 \quad (7)$$

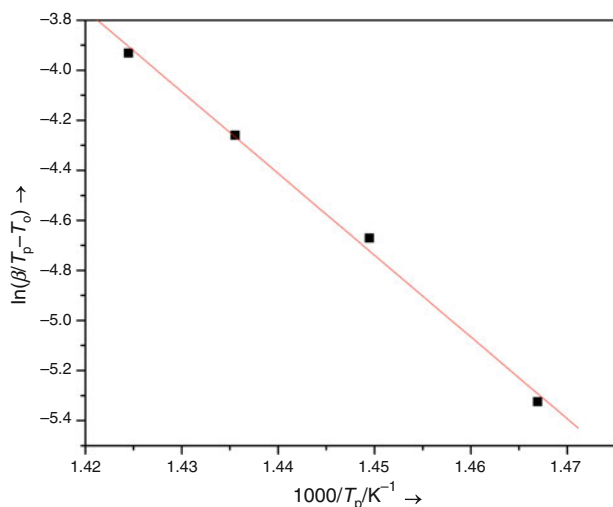
where  $T_p$  and  $T_o$  are the peak and the onset temperatures of crystallization, respectively. The values of  $E$  and  $k_0$  obtained from the plot  $(\ln(\beta/(T_p - T_o)))$  vs.  $1000/T_p$  (Fig. 4) are given in Table 2.



**Fig. 3** Kissinger plot

**Table 2** Activation energy ( $E$ ) and pre-exponential factor ( $k_0$ ) derived using various methods

Method	$E/\text{kJ mol}^{-1}$	$k_0/\text{s}^{-1}$
Kissinger	$259.9 \pm 2$	$4.86 \times 10^{17}$
Ozawa	$258.1 \pm 2$	–
Augis and Bennett	$271.7 \pm 1$	$3.33 \times 10^{18}$
Boswell	$256.4 \pm 2$	–
Gao and Wang	$278.4 \pm 3$	–

**Fig. 4** Augis and Benett plot**Table 3** Values of Avrami exponent ( $n$ ) from different methods

Heating rate	Augis and Bennett	Matusita and Sakka
4	2.5	2.7
6	3.5	2.9
8	3.1	2.9
10	2.8	3.0

Further,

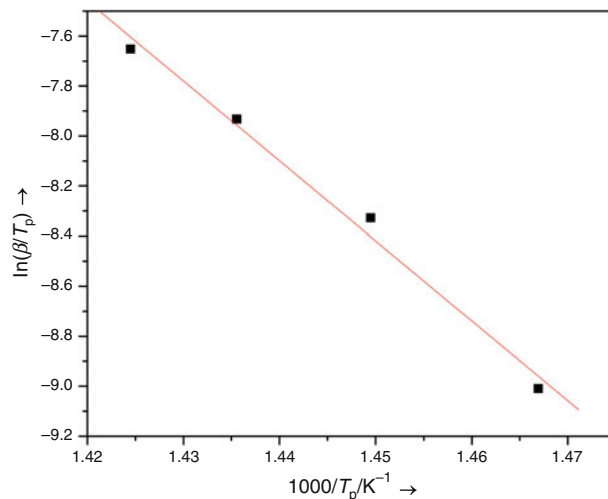
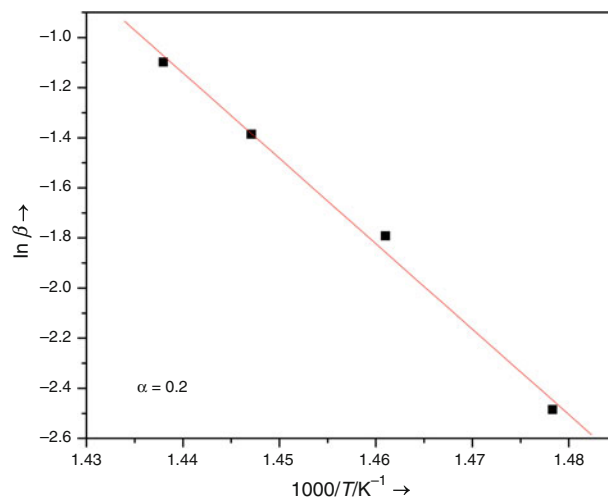
$$n = 2.5 \frac{T_p^2}{\Delta T \left(\frac{E}{R}\right)} \quad (8)$$

where  $\Delta T$  is the full width at half maximum of the DSC curve.  $n$  derived using Eq. 8 is given in Table 3.

(iii) *Boswell method*: Boswell method [19] determines the activation energy at peak temperature (Table 2) using the following equation

$$\ln\left(\frac{\beta}{T_p}\right) = -\frac{E}{RT_p} + \text{const} \quad (9)$$

Plot of  $\ln(\beta/T_p)$  vs.  $1000/T_p$  (Fig. 5) gives the activation energy  $E$  listed in Table 2.

**Fig. 5** Boswell plot**Fig. 6** OFW plot  $\alpha = 0.2$ 

*Ozawa–Flynn–Wall (OFW) method* In this method [20, 21] the temperature integral in Eq. 4 is simplified by using the Doyle's approximation [22–24] and hence we obtain the following equation:

$$\ln \beta = -1.0516 \frac{E(\alpha)}{RT_x} + \text{const} \quad (10)$$

The plot of  $\ln \beta$  vs.  $1/T_x$  (Fig. 6) gives the slope  $-1.0516 E(\alpha)/R$  from which the activation energy has been evaluated (Table 1). At  $T_x = T_p$ , (Ozawa method) the value of  $E$  determined (from Fig. 7) using Eq. 10 is given in Table 2.

*Linear differential isoconversional method*

The method suggested by Friedman [25] sometimes known as transformation rate-isoconversional method, utilizes the differential of the transformed fraction and hence it is

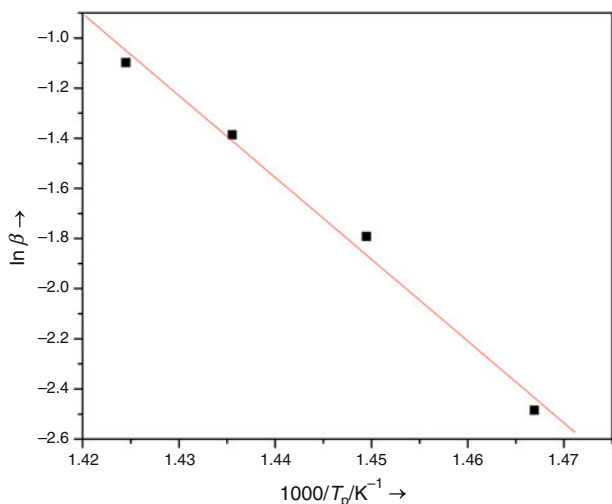


Fig. 7 Ozawa plot

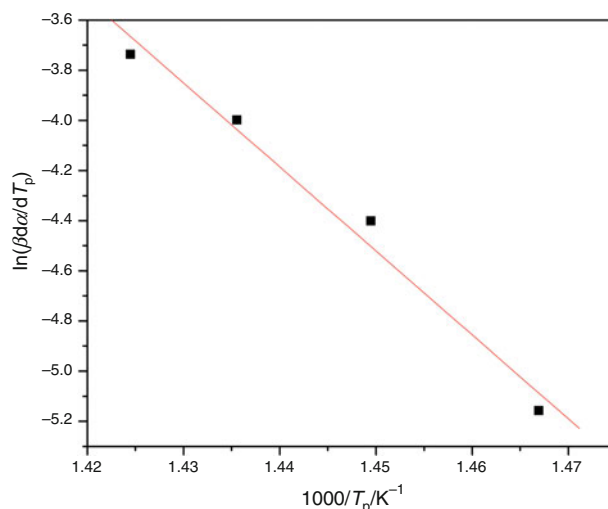


Fig. 9 Gao and Wang plot

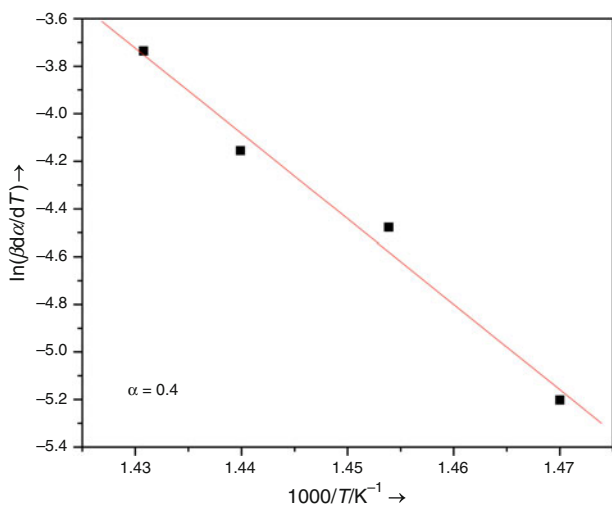


Fig. 8 Friedman plot  $\alpha = 0.4$

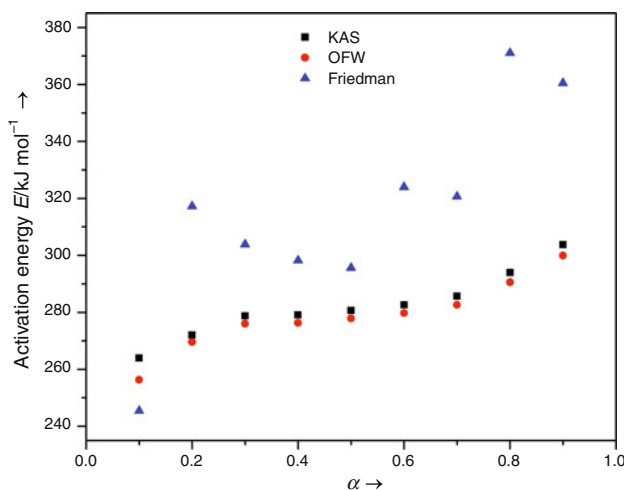


Fig. 10 Local activation energy  $E$  at different  $\alpha$  from different methods

called differential isoconversional method. Substituting value of  $k(T)$  in Eq. 3 Friedman derived a linear differential isoconversional expression as

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln\beta\left(\frac{d\alpha}{dT}\right)_\alpha = \ln(Af(\alpha)) - \frac{E_\alpha}{RT_\alpha} \quad (11)$$

by taking logarithm on both sides of Eq. 3. For a constant  $\alpha$ , the plot of  $\ln\left(\beta\frac{d\alpha}{dT}\right)$  vs  $\left(\frac{1}{T}\right)$  should be a straight line (Fig. 8) whose slope gives us the value of  $E$ .

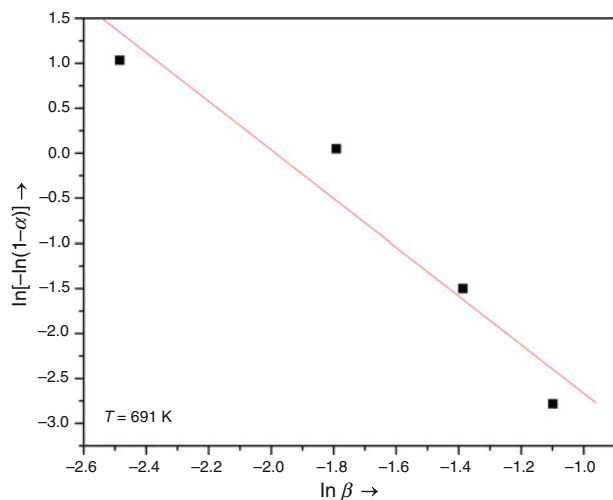
Since this method does not take any mathematical approximation for the temperature integral, it is considered to give accurate estimate of  $E$ . Thus the method does not require any assumption on  $f(\alpha)$ , i.e., it is a so-called model-free method. However, being a differential method, its accuracy is limited by the signal noise.

A method suggested by Gao and Wang [26] is a special case of the Friedman method. This method uses the following expression to determine the activation energy. The value of activation energy obtained is given in Table 2.

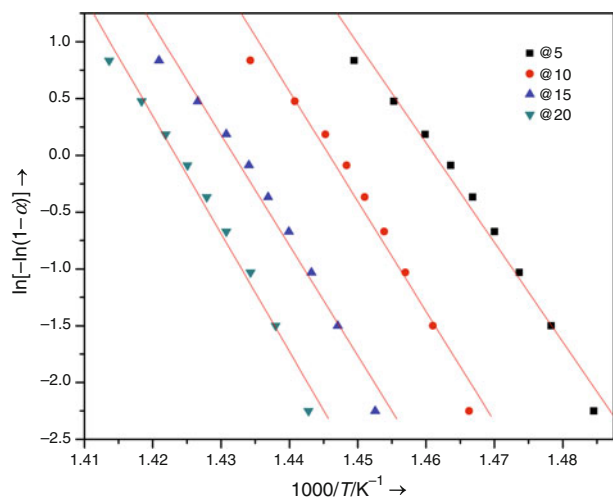
$$\ln\left(\beta\frac{d\alpha}{dT_p}\right) = -\frac{E}{RT_p} + \text{const} \quad (12)$$

A plot of  $\ln\left(\beta\frac{d\alpha}{dT_p}\right)$  vs.  $\left(\frac{1}{T_p}\right)$  is given in Fig. 9.

The values of local activation energy  $E_\alpha$  as a function of  $\alpha$  has been given in Table 1 using three different isoconversional methods namely, KAS, OFW, and Friedman. This result has also been shown graphically in Fig. 10. It appears from this graph that results obtained using KAS and OFW methods lie quite close to each other while Friedman points are quite scattered.



**Fig. 11** Plot of  $\ln[-\ln(1 - \alpha)]$  vs.  $\ln \beta$  at  $T = 691$  K



**Fig. 12** Plot of  $\ln[-\ln(1 - \alpha)]$  vs.  $1000/T$  for different heating rates

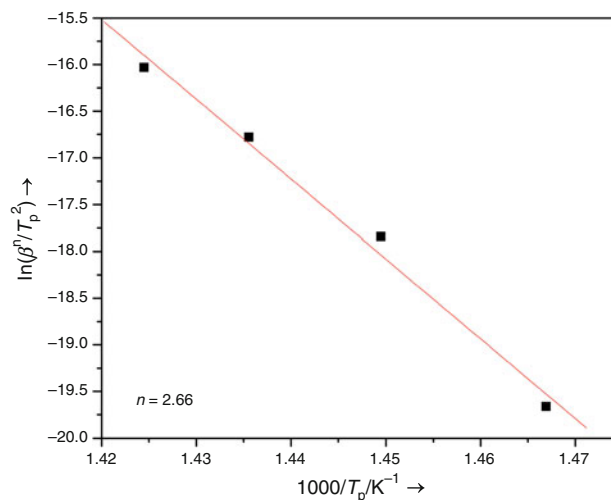
### Isokinetic methods

#### Matusita and Sakka method

Matusita and Sakka [27] suggested the following equation specifically for the non-isothermal data

$$\ln[-\ln(1 - \alpha)] = -n \ln \beta - \frac{mE}{RT} + \text{const.} \quad (13)$$

where  $m$  is an integer depends on the dimensionality of the crystal and the Avrami exponent  $n$  depends on the nucleation process. For a constant temperature, the plot of  $\ln[-\ln(1 - \alpha)]$  vs.  $\ln \beta$  gives a straight line (Fig. 11) and the slope gives the value of  $n$ . Here we have taken seven different constant temperatures and the average value of  $n$  comes out to be 2.66. The plot of  $\ln[-\ln(1 - \alpha)]$  vs.  $1/T$  at constant heating rate should be a straight line and the value



**Fig. 13** Modified Kissinger plot for  $n = 2.66$

of  $m$  is obtained from the slope (Fig. 12). Different values of  $n$  are derived from these  $m$  values by using  $n = (m + 1)$  and are given in Table 3.

#### Modified Kissinger method

The modified Kissinger equation [28] given below can be utilized to derive the activation energy ( $E$ ).

$$\ln\left(\frac{\beta^n}{T_p^2}\right) = -\frac{mE}{RT_p} + \text{const} \quad (14)$$

where  $E$  is the activation energy for crystallization,  $T_p$  is the peak temperature, and  $R$  is the universal gas constant.  $m$  is known as the dimensionality of growth and for the sample without preannealing treatment,  $m = (n - 1)$ . In order to derive  $E$  from this equation, one must know the value of  $n$ . The  $n$  value can be obtained from the slope of the plot of  $\ln[-\ln(1 - \alpha)]$  vs.  $\ln \beta$  at constant temperature. In order to evaluate  $E$ , the average value of  $n = 2.66$  is substituted in Eq. 14. Then the plot of  $\ln\left(\frac{\beta^n}{T_p^2}\right)$  vs.  $\frac{1}{T_p}$  (Fig. 13) gives the values of activation energy  $E$ , which is 428.12 kJ/mol.

### Conclusions

Both model dependent isokinetic and model-free isoconversional methods have been utilized to study the crystallization kinetics of the first peak of the crystallization process involved in the presently taken system namely  $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$  metallic glass. The isokinetic methods, though model dependent, provide single value of activation energy. Besides, they also provide Avrami exponent  $n$ , which gives an idea about the dimensionality

of the growth of crystals. Isoconversional techniques, on the other hand, provide quite accurate values of  $E_\alpha$  as a function of  $\alpha$  as these analytical methods are supposed to be model free. It is obvious from the results obtained through KAS and OFW equations that activation energy initially increases with  $\alpha$ . However, from  $\alpha = 0.4$  to  $0.5$ , there is an incremental increase in  $E_\alpha$ . Thereafter,  $E_\alpha$  increases again with  $\alpha$ . This interesting result is an indication of the fact that even before first step of crystallization is completed, second step starts. The activation energy,  $E$  obtained using the Friedman method, on the other hand, show appreciable variation and there is no systematic trend. This is attributed to the signal noise involved [29]. It is also noteworthy that the activation energy values using various isoconversional methods and the special cases of isoconversional techniques namely Kissinger, Ozawa, Augis and Bennett, Boswell, and Gao and Wang are quite consistent, whereas modified Kissinger method overestimates it. The isoconversional approach has been utilized to obtain the dependence of activation energy on transformed fraction for few Fe-based multicomponent amorphous alloys [30]. Various forms of the conversion function have been used and Sestak–Berggren function in temperature-programmed reduction has been recently reported [31].

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