

ISOCONVERSIONAL vs. MODEL FITTING METHODS

A case study of crystallization kinetics of a Fe-based metallic glass

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The crystallization of metallic glasses has been studied quite extensively using differential scanning calorimetry (DSC) technique. Most methods rely on isokinetic hypothesis for the kinetic analysis of crystallization for which the choice of a reliable model is very important. Due to inherent uncertainty in the determination of kinetic parameters, the model-free isoconversional analytical techniques were proposed. However, these isoconversional methods are scarcely used for metallic glasses. In the present work, the crystallization kinetics of Fe₆₇Co₁₈B₁₄Si₁ metallic glass through both isoconversional and isokinetic methods has been investigated and attention has been focused on the relative applicability of the two methods.

Keywords: crystallization kinetics, isoconversional methods, metallic glasses, model fitting methods

Introduction

The transformation rate for a solid state reaction is generally assumed in innumerable publications as the product of two functions, one depending only on the temperature T and the other depending only on the fraction transformed α [1].

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) f(\alpha) \quad (1)$$

where α is the degree of conversion, T , the temperature, β , the linear heating rate, and $f(\alpha)$, the differential conversion function (reaction model). $k(T)$ is a temperature dependent function given by the Arrhenius equation

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

with A being the pre-exponential factor and E , the activation energy and R , the gas constant.

For non-isothermal experiments, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the determination of kinetic triplet $f(\alpha)$, A and E is an interlinked problem [2]. In order to determine this triplet, various methods have been worked out. These methods can, in general, be categorized as: (i) isoconversional and (ii) isokinetic. The isoconversional methods require the knowledge of temperatures $T_\alpha(\beta)$ at which an equivalent stage of reaction occurs for various heating rates. The equivalent stage is defined as the stage at which a fixed amount is transformed or at which a fixed fraction of the total amount is trans-

formed [3]. These methods can, further, be classified into two groups [4, 5]. One set of method depends on approximating the temperature integral and requires data on $T_\alpha(\beta)$. Hence these are called integral isoconversional methods like those proposed by Kissinger [6], Ozawa [7], Augis and Bennett [8], Bosewell [9], Ozawa–Flynn–Wall (OFW) [7, 10], Kissinger–Akahira–Sunose (KAS) [6, 11] and Li and Tang [12]. Second set of isoconversional methods depends on the rate of transformation at $T_\alpha(\beta)$ as well as the data on $T_\alpha(\beta)$ [13]. These methods are referred to as differential methods like those given by Friedman [14] and Gao and Wang [15]. The isoconversional methods, being model-free, are considered to give accurate values of the kinetic parameters such as the activation energy and the pre-exponential factor. However, recently it has been shown, that model-free kinetics approach rests primarily on evaluating the dependence of activation energy on fractional conversion [16] and is not concerned with evaluating A , $g(\alpha)$ or $f(\alpha)$, because they are not needed for performing kinetic predictions.

The isokinetic methods of kinetic analysis depend on the reaction model. It also assumes the Arrhenius temperature dependence of the rate constant $k(T)$. Recently non-Arrhenius temperature dependence of rate constant has also been investigated [17]. Model fitting methods do not achieve a clean separation between the temperature dependent $k(T)$ and the reaction model $f(\alpha)$. Moreover, the temperature sensitivity of the reaction rate depends on the extent

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of conversion. As a result, these methods are considered to be approximate. Among the various methods of this type, we have used the Coats and Redfern (CR) method [18] and the invariant kinetic parameters (IKP) method [19, 20].

Present investigations focus on the applicability of the two types of methods for the determination of activation energy of crystallization of a Fe-base metallic glass.

Experimental

Specimens of amorphous $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$ (2605CO) ribbons, prepared by single roller melt spinning technique were procured from Allied Corporation, USA. The amorphous nature of ribbons was confirmed by XRD and TEM. 2–3 mg of the as-quenched samples of $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$ ribbons were heated in DSC (DSC-50, Shimadzu, Japan) in crimped aluminium pan at four linear heating rates (4, 8 10 and 16 K min^{-1}) from room temperature to 720 K in air. DSC scans were recorded by a thermal analyzer (TA-50 WSI, Shimadzu, Japan) interfaced to a computer. The detection sensitivity of the instrument is $\sim 10 \mu\text{W}$.

Results and discussion

DSC curves of the linear heating experiments at four different heating rates are shown in Fig. 1. The curves show two-stage crystallization. It can be observed that the crystallization peaks shift to higher temperatures with increasing heating rates. This shift in the peak forms the basis for determination of the activation energy using the well-known Kissinger method (discussed below). Due to increase in the sensitivity, the peak height also increases with increasing heating rate.

The non-isothermal crystallization data of DSC have been analyzed using different methods of kinetic analysis mentioned in the aforementioned introduction.

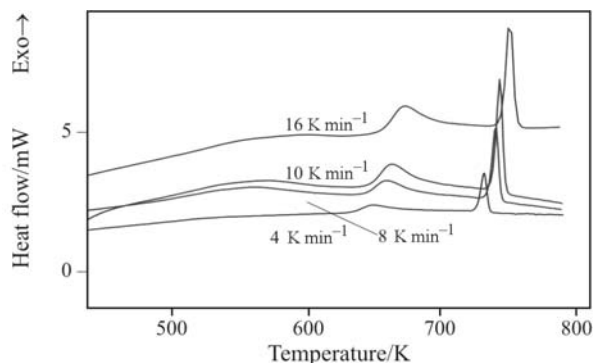


Fig. 1 DSC curves of the metallic glass 2605CO at different heating rates

Isoconversional analysis

Isoconversional methods evaluate the activation energy values at progressive degrees of conversion E_α without modelistic assumptions. The isoconversional methods suggested by Ozawa and Flynn and Wall use approximations of the evaluation of the integral appearing in the rate equation, whereas the method suggested by Friedman uses a differential form of the rate equation which leads to simple linear equations for evaluating the activation energy. Analysis of errors introduced by such approximations has been performed by Vyazovkin and Dollimore [21] who introduced a non-linear isoconversional method to increase the accuracy of evaluating the activation energy.

Linear integral isoconversional methods

Kissinger–Akahira–Sunose (KAS) method

This method is based on the expression

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT} \quad (3)$$

This is classified as an isoconversional method as we plot $\ln(\beta/T^2)$ vs. $1000/T$ for constant conversion, α (Fig. 2). Using this expression one gets the local activation energy $E(\alpha)$ at particular α value (Table 1).

The following discussion describes some of the methods available in the literature which are basically special cases of the KAS equation (3).

• 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 (α) at T_p . In many cases, the extent of conversion (α_p) at T_p varies with the heating rate and hence raises doubt about grouping this method into isoconversional category. However, in the present study, the analysis of the crystallization data shows that α_p is nearly constant and we can group it as a special case

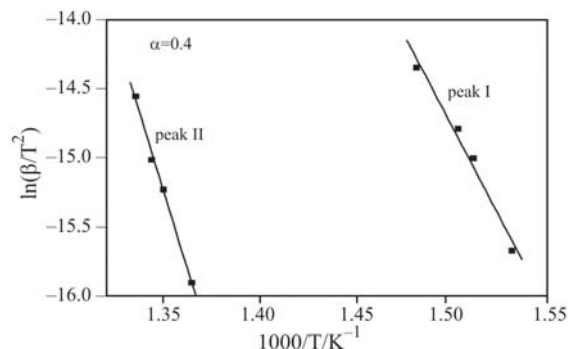


Fig. 2 KAS plot (Eq. (3))

Table 1 Local activation energy (E) at different extent of conversion using different methods

α	$E/\text{kJ mol}^{-1}$					
	OFW		KAS		Friedman	
	Peak I	Peak II	Peak I	Peak II	Peak I	Peak II
0.1	225±2	386±1	226±2	394±1	238±4	–
0.2	232±1	377±2	233±1	384±2	221±5	428±1
0.3	230±2	378±2	231±2	385±2	219±6	402±4
0.4	220±3	370±2	220±3	377±2	208±8	423±7
0.5	214±3	366±1	214±3	376±1	200±8	399±4
0.6	217±4	361±1	217±4	367±1	220±9	382±6
0.7	214±4	358±1	214±4	364±1	224±9	374±5
0.8	224±5	358±1	224±5	364±1	236±10	399±8
0.9	223±5	348±2	223±5	354±2	195±9	295±1

of KAS isoconversional method. The Kissinger equation [6] is

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left(\frac{AR}{E}\right) \quad (4)$$

The so-obtained activation energy and the pre-exponential factor A are listed in Table 2. This method provides the value of A apart from the value of activation energy E . Here one gets single value of E using Eq. (4).

- Bosewell method: In order to determine the activation energy this method [9] uses the following equation

$$\ln\left(\frac{\beta}{T_p}\right) = -\frac{E}{RT_p} + \text{const} \quad (5)$$

The slope of the graph $\ln\frac{\beta}{T_p}$ vs. $\frac{1}{T_p}$ gives the activation energy as shown in Table 2. However, this equation does not provide any information about the frequency factor (A) and single E value is obtained like Kissinger method.

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

Method	$E/\text{kJ mol}^{-1}$		A/s^{-1}	
	Peak I	Peak II	Peak I ($\cdot 10^{15}$)	Peak II ($\cdot 10^{22}$)
Kissinger	220±1	349±1	1.75	3.4
Ozawa	226±2	354±3	–	–
Augis and Bennett	227±1	354±4	4.3	9.8
Bosewell	227±1	355±1	–	–
Gao and Wang	211±5	370±10	0.33	–
IKP	188±55	293±2	–	–

- Augis and Bennett's method: According to the method suggested by Augis and Bennett [8],

$$\ln\left(\frac{\beta}{T_p - T_0}\right) = -\frac{E}{RT_p} + \ln A \quad (6)$$

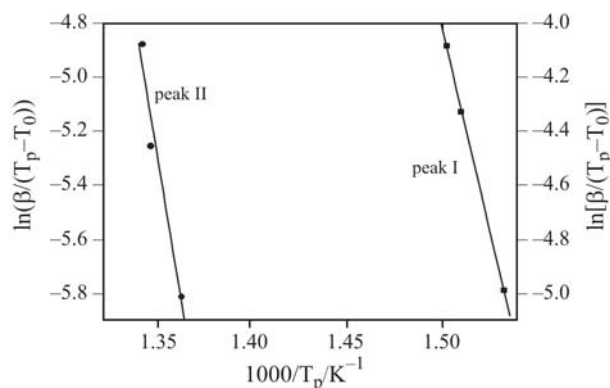
where T_p and T_0 are the peak temperature and the onset temperature respectively. The values of E and A obtained from the plot ($\ln(\beta/(T_p - T_0))$ vs. $1000/T_p$) (Fig. 3) are given in Table 2.

Ozawa–Flynn–Wall (OFW) method

This method involves the measurement of the temperature T_α , corresponding to a fixed value of fractional crystallization, α , from the experiments at different heating rates, β . The OFW method is based on the following equation:

$$\ln\beta = -1.0516 \frac{E(\alpha)}{RT_\alpha} + \text{const} \quad (7)$$

The plot of $\ln\beta$ vs. $1000/T_\alpha$ gives the slope $-1.0516E(\alpha)/R$ from which the activation energy has


Fig. 3 Augis and Bennett plot (Eq. (6))

been evaluated (Table 1). At $T_\alpha = T_p$, the value of E determined using Eq. (7) is given in Table 2.

Li–Tang method

According to method suggested by Li and Tang [12], from Eq. (1) we get,

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln[Af(\alpha)] \quad (8)$$

or

$$\int_0^\alpha \ln\left(\frac{d\alpha}{dt}\right) d\alpha = G(\alpha) - \frac{E}{R} \int_0^\alpha \left(\frac{1}{T}\right) d\alpha \quad (9)$$

where

$$G(\alpha) \equiv \alpha \ln A + \int_0^\alpha \ln f(\alpha) d\alpha \quad (10)$$

has the same value for a given reaction under study and a given α irrespective of β . A plot of $\int_0^\alpha \ln\left(\frac{d\alpha}{dt}\right) d\alpha$ vs. $\int_0^\alpha \left(\frac{1}{T}\right) d\alpha$, for a set of β 's at constant conversion α will have the slope $-E/R$ (Fig. 4).

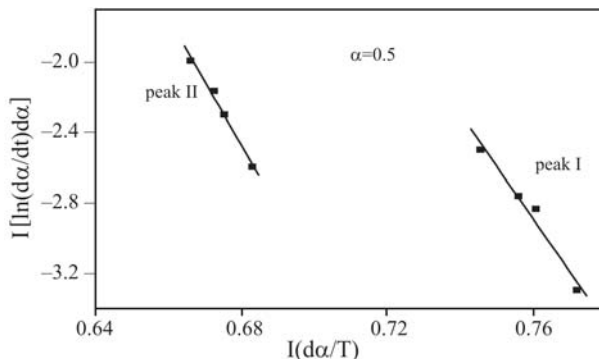


Fig. 4 Li Tang plot (Eq.9)

Linear differential isoconversional methods

The differential isoconversional method suggested by Friedman is based on Eq. (1) that leads to;

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT} \quad (11)$$

For a constant α , the plot of $\ln\left(\beta \frac{d\alpha}{dT}\right)$ vs. $\left(\frac{1}{T}\right)$

obtained from curves recorded at several heating rates should be a straight line whose slope gives us the value of E . The values of E at different α , obtained using three different methods are listed in Table 1.

A method suggested by Gao and Wang [15] is a special case of the Friedman method. This method uses the following expression to determine the activation energy and frequency factor.

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

$$K_p = \frac{\beta E}{RT_p^2} \quad (13)$$

where

$$K_p = A \exp\left(\frac{-E}{RT_p}\right)$$

The activation energy obtained from the plot of $\ln\left(\beta \frac{d\alpha}{dT}\right)_p$ vs. $\frac{1}{T_p}$ is given in Table 2.

Non-linear integral isoconversional method

An advanced isoconversional method has been recently described by Vyazovkin [22]. As all other isoconversional methods, this method is based on the assumption that the reaction model, $g(\alpha)$ is independent of the heating program. So, for any two experiments conducted at different heating rates the ratio of the temperature integral $I(E, T_\alpha)$ to the heating rate β is a constant. For a given conversion and a set of n experiments performed under different heating rates, the activation energy can be determined at any particular value of α by finding the value of E_α for which the function

$$\sum_{i \neq j}^n \sum_{i \neq j}^n \frac{[I(E_\alpha, T_{\alpha i})\beta_j]}{[I(E_\alpha, T_{\alpha j})\beta_i]} \quad (14)$$

is a minimum. The minimization procedure is repeated for each value of α to find the dependence of activation energy on the extent of conversion. Using this procedure we have processed our non-isothermal experimental data and the results are shown in graphs (Figs 5 and 6).

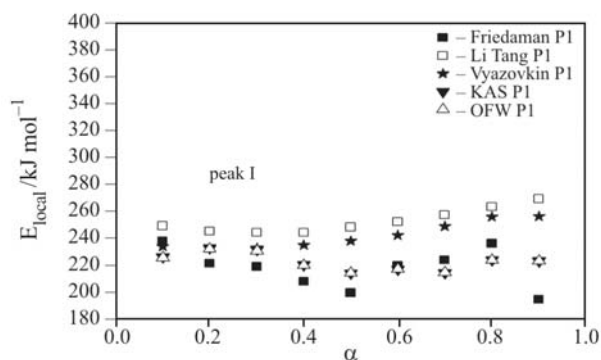


Fig. 5 Local activation energy E at different α from different methods for peak I

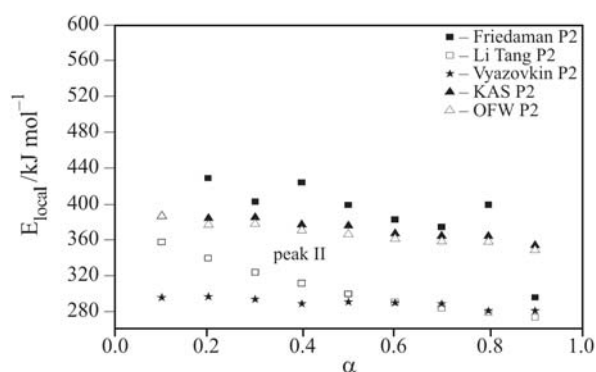


Fig. 6 Local activation energy E at different α from different methods for peak II

Model fitting methods

Though the model-fitting methods are known for their simplicity in providing the kinetic triplet (i.e. frequency factor A , activation energy E and the reaction model $f(\alpha)$), they suffer from several problems such as their inability to establish a unique reaction model. On the other hand, it is difficult to get an idea about the reaction model with the help of the model-free isoconversional methods which provide accurate estimates of E . It has been recently demonstrated that the complementary use of the model-free method with the isoconversional methods is very useful to understand the solid-state reaction kinetics [23]. One of the most popular model-fitting methods is the Coats and Redfern method [18]. This method is based on the equation

$$\ln \frac{g_i(\alpha)}{T^2} = \ln \left[\frac{A_i R}{\beta E_i} \left(1 - \frac{2RT}{E_i} \right) \right] - \frac{E_i}{RT} \quad (15)$$

$$\cong \ln \frac{A_i R}{\beta E_i} - \frac{E_i}{RT}$$

The graph of $\ln \frac{g_i(\alpha)}{T^2}$ vs. $\frac{1}{T}$ gives a straight line

whose slope and intercept allow us to calculate E and A for a particular reaction model. In the present study, this method is used to analyze the first crystallization peak. For the kinetic models listed in Table 3 and for $0.05 \leq \alpha \leq 1$, the straight lines corresponding to CR method are characterized by correlation coefficients (r). The general practice in this method to determine E is to look for the model corresponding to maximum r . In some cases, the so-obtained value of E is significantly different from those obtained from other methods. For example, in the present case, r is maximum for the model $-\ln(1-\alpha)$. But the corresponding E is high compared to those obtained using different isoconversional methods. Thus, using statistical criterion it is difficult to say which model is the real one. For such cases an r value lower than r_{\max}

could correspond to the true kinetic model [24]. The true analytical form of the conversion function can be determined from the activation energy for a single $\alpha=\alpha(T)$ curve that equals the activation energy obtained by means of isoconversional methods. By applying this criterion for the analyzed data $g(\alpha)=1-(1-\alpha)^{1/3}$ is found to be more suitable for the description of the solid-state reaction.

The invariant kinetic parameter (IKP) method

It has been observed that the same experimental curve $\alpha=\alpha(T)$ can be described by different function of conversion ($f(\alpha)$). Further, the values of the activation energy obtained for various $f(\alpha)$ for single non-isothermal curve are correlated through the compensation effect [25]. These observations form the basis of the IKP method. In order to apply this method, $\alpha=\alpha(T)$ curves are obtained at different heating rates (β , $v=1, 2, 3, \dots$) using DSC. For each heating rate the pairs (A_{vj} , E_{vj} , where j corresponds to a particular degree of conversion, are determined using the following equation:

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (16)$$

For constant β , a plot of $\ln \frac{g(\alpha)}{T^2}$ vs. $\frac{1}{T}$ is a straight line whose slope allows the evaluation of activation energy E_v and intercept, pre-exponential factor, A_v for different reaction models $g(\alpha)$. The same procedure is repeated to obtain the pairs (E_v , A_v) for different heating rates. Now, the calculation of invariant activation parameters is done using the compensation relation

$$\ln A_v = \alpha^* + \beta^* E_v \quad (17)$$

The above Eq. (17) represents a linear relationship between $\ln A$ and E ; any increase in the magnitude of one parameter is offset, or compensated, by appropriate increase of the other. Plotting $\ln A_v$ vs. E_v for different heating rates, the compensation effect parameters α^* and β^* are obtained. These parameters follow an equation [26]

$$\alpha^* = \ln A - \beta^* E \quad (18)$$

The plot of α^* and β^* gives the true values of E and A (Table 2).

Conclusions

Present study suggests that the model-free isoconversional methods are definitely superior to the iso-kinetic ones for the accurate determination of kinetic parameters like E and A . However, the knowledge of accurate E

Table 3 Values of kinetic parameters obtained for various reaction models by means of CR method

Model	4 K min ⁻¹			8 K min ⁻¹			10 K min ⁻¹			16 K min ⁻¹		
	E/ kJ mol ⁻¹	lnA	r	E/ kJ mol ⁻¹	lnA	r	E/ kJ mol ⁻¹	lnA	r	E/ kJ mol ⁻¹	lnA	r
1-(1- α) ^{1/3}	212±0.8	25±1.3	0.961	230±1	28±1.5	0.95	224±0.9	27±1.3	0.958	185±0.9	20±1.3	0.943
1-(1- α) ^{1/2}	195±0.9	22±1.3	0.952	207±1	24±1.6	0.937	202±0.9	23±1.4	0.946	167±0.9	17±1.3	0.929
(1-(1- α) ^{1/3}) ²	436±1.7	65±2.5	0.963	471±2	71±3	0.952	457±1.8	68±2.7	0.96	382±1.8	54±2.6	0.946
-ln(1- α)	253±0.8	34±1.2	0.976	282±0.9	39±1.4	0.972	274±0.8	38±1	0.978	229±0.9	29±1.2	0.967
(-ln(1- α)) ^{1/4}	55±0.3	-4±0.3	0.968	62±0.2	-2±0.3	0.964	58±0.2	-2±0.3	0.972	48±0.2	-4±0.3	0.955
(-ln(1- α)) ^{1/3}	77±0.3	1±0.4	0.971	87±0.3	3±0.5	0.967	83±0.3	3±0.4	0.974	69±0.3	-0.2±0.4	0.96
(-ln(1- α)) ^{1/2}	121±0.4	9±0.9	0.974	136±0.5	12±0.7	0.97	131±0.4	11±0.6	0.976	108±0.4	7±0.6	0.964

and A using thermal analysis, is not sufficient for the detailed investigations of the dimensionality of the growth and the grain size involved in the process of crystallization. Information from kinetic studies must be combined [27] with information derived from a variety of other techniques to permit a meaningful description of events corresponding to the conversion of reactants [glass] to products [crystals].

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