Journal of Non-Oxide Glasses Vol. 1, No. 2, 2009, p. 103-111

An integrated approach for determining the crystallization kinetics parameters of a glassy system

A.S. Soltan

Physics Department, Faculty of Science, Assiut University,71516 Assiut, Egypt

The applicability of the kinetic analysis of data obtained by non-isothermal differential scanning calorimetry (DSC) is discussed. Using different heating rates, the crystallization kinetic parameter of a glassy system can be calculated in sequences. Theses parameters include the activation energy of crystallization E (KJ/mol), the kinetic exponent or the reaction order of crystallization n, and the pre-exponential coefficient of effective overall reaction or the frequency factor $K_o(s^{-1})$. At different heating rates B_i (K/min), the volume fractions of crystallization $\chi_i(t)$ are calculated. Next, the data of temperature T_i (K) and the time t_i (s), which used for determining E, can be evaluated at the same values of $\chi_i(t)$ at different heating rates. Finally, the values of n and K are determined from the intercept of the straight line relation between ($\ln t_i$) versus ($1/T_i$). The validity of application of this technique has been tested on computer simulated crystallization curves.

(Received April 28, 2009; accepted June 10, 2009)

Keywords: Amorphous materials; Kinetics; Calorimetry; Thermal analysis

1. Introduction

Crystallization of chalcogenide glasses plays an important role in determining the thermal stability. The kinetics of phase transformations is important in physics, chemistry, metallurgy, ceramic and materials sciences. Thermal analysis is one of common experimental techniques used for studying theses transformations [1]. Various techniques have been applied to determine the kinetics of first order phase transformations, e.g. the crystallization of amorphous materials. Calorimetric methods, and in particular differential scanning calorimetry (DSC), are widely used for study of the kinetics of such processes. Theses methods offer advantages, e.g, they are quite sensitive, not demanding with regard to sample preparation, and relatively independent of the sample geometry [2]. DSC measures a volume fraction transformed as a function of time (isothermal DSC) or temperature (non-isothermal) by measuring the heat released or absorbed during a phase change. In recent years, especially non-isothermal DSC measurements have become very attractive for the study of phase transformations. Non-isothermal experiments can be performed more rapidly than isothermal ones, and they can also be used to extend the temperature range of measurements beyond that accessible in isothermal experiments. Industrial processes often depend on the kinetic behavior of system undergoing phase transformations under non-isothermal conditions. In this respect, a definite measurement of non-isothermal transformations kinetics is desirable [3].

Studies of the crystallization kinetics using only one experimental point from each of the DSC curve corresponding to one heating rate has been discussed [4-8]. Other techniques take into consideration a large number of values obtained from the entire experimental curve for each of the different heating rates, with varying results depending on the nature of the glass alloys under studies [9-12].

The aim of the present work is to determine the most important crystallization kinetic parameters which include, the crystallization activation energy E, the frequency factor K_o, and the reaction order of crystallization n, under non-isothermal conditions without any approximations in addition to those involved in obtaining Johnson-Mehl-Avrami (JMA) theoretical model [13]. To realize this aim, The validity of application of the present technique has been tested on computer simulated crystallization curves.

2. Theoretical basis

The general theory of transformations kinetics was derived for transformation conditions [14]. Numerous methods have been developed for the treatment of non-isothermal DSC data and predict the behavior of the system under different conditions [13,15,16].

The theoretical basis for interpreting DTA or DSC data is provided by the formal theory of transformations kinetics or chemical as the volume fraction $\chi(t)$ crystallized (transformed or interacted) in time (t), using the Johnson-Mehl-Avrami (JMA) formalism [17-20].

$$\mathbf{x(t) = 1 - exp\left[- (Kt)^{n}\right]} \tag{1}$$

Where K is the rate constant which has an Arrhenius temperature dependence [21]

$$\mathbf{K(T) = K_{0}\, exp\left[- (E / RT)\right]} \tag{2}$$

Where K_0 is the rate constant or the pre-exponential coefficient of effective overall reaction rate, R (JK^{-1}) the gas constant and T (K) the absolute temperature.

In equation (2), E is the effective activation energy describing the overall crystallization process, and under non-isothermal transformation kinetics, Henderson [15] has shown that, JMA formalism can be used under specific restrictions that limit the applicability of this formalism to 'site saturation' transformation only. In this case, nucleation takes place at the very start of the transformation, and the nucleation rate is

$B(=dT/dt)$

$$T = T_o + B\,t \tag{3}$$

where T_o (K) is the on-set temperature of crystallization.

3. The sequential determination of the crystallization kinetic parameters

Let us consider equal values of fraction crystallized (χ_i), are given at different heating rates B_1, B_2, B_3, etc. Therefore, equation (1) may be rewritten several times as:

$$1 - x_i = \exp\left[-(K_i t_i)^n\right] \tag{4}$$

and K_i is given as:

$$K_i(T) = K_o \exp\left[-(E/RT_i)\right] \tag{5}$$

,
where T_i(K) and t_i (s) are the temperature and time corresponding to the fraction of crystallization χ_i which is given at heating rate B_i (K/min). Taking the logarithm of equation (4) one obtains:

$$\ln(1 - x_i) = -(K_i t_i)^n \tag{6}$$

which may be rewritten in the form:

$$\left[-\ln\left(1 - x_i\right)\right]^{1/n} = K_i t_i \tag{7}$$

.
Now, using equation (5) in equation (7) to obtain:

$$\left[-\ln\left(1 - x_i\right)\right]^{1/n} / K_o = t_i \exp\left(-E/RT_i\right) \tag{8}$$

If we considered
.

$$\theta_i = \frac{\left[-\ln\left(1 - x_i\right)\right]^{1/n}}{K_o} \tag{9}$$

Then, equation (8) may be rewritten as:

$$t_i = \theta_i \exp\left(E/RT_i\right) \tag{10}$$

3.1. Crystallization activation energy, E

Taking the logarithm of equation (10) one may obtains:

$$\ln(t_i) = (E/R)(1/T_i) + \ln\theta_i \tag{11}$$

Equation (11) represents a relation of straight line between (ln t_i) versus ($1/T_i$), the slope of which equal to (E/R) and the intercept of which equal to (ln θ_i). The activation energy E (kJ/mol) may be obtained from the slope of the relation between (ln t_i) versus ($1/T_i$).

3.2. Reaction order, n

This parameter reflects the nucleation and growth morphology and can be obtained from the intercept of equation (11), that are obtained at two different values of the fraction $\chi_i(t)$. Therefore, if we supposed two different fractions x_a and x_b, then from equation (9) and equation (11) one may writes the intercept of equation (11) two times as:

$$\ln\theta_a = \ln\left\{\frac{[-\ln(1-x_a)]^{1/n}}{K_o}\right\} \tag{12}$$

$$\ln\theta_b = \ln\left\{\frac{[-\ln(1-x_b)]^{1/n}}{K_o}\right\} \tag{13}$$

Making the appropriate mathematical treatments of equations (12) and (13); then one may obtains:

$$A = \frac{\exp(\ln\theta_a)}{\exp(\ln\theta_b)} = \frac{\theta_a}{\theta_b} = \left[\frac{\ln(1-x_a)}{\ln(1-x_b)}\right]^{1/n} \tag{14}$$

Let us consider

$$D = \frac{\ln(1-x_a)}{\ln(1-x_b)} \tag{15}$$

Then equation (14) may be rewritten as:

$$A = [D]^{1/n} \tag{16}$$

The value of n is then given as:

$$n = \frac{\log[\ln(1 - x_a)/\ln(1 - x_b)]}{\log[\exp(\ln\theta_a - \ln\theta_b)]} \tag{17}$$

3.3. The frequency factor, K_0

K_o is related to molecular collisions probability which represent the pre-exponential coefficient of effective overall reaction rate and can be determined by reconsidering equation (12) or (13). Taking the exponential of equation (12), one givin:

$$\exp(\ln\theta_a) = \frac{[-\ln(1 - x_a)]^{1/n}}{K_o} \tag{18}$$

which may be written as:

$$K_o = \frac{[-\ln(1 - x_a)]^{1/n}}{\exp(\ln\theta_a)} \tag{19}$$

Here, the value of *n* is known, and other parameters involved in this equation can be obtained from the experimental data. Similarly, from equation (13), the value of K_o may be obtained as:

$$K_o = \frac{[-\ln(1 - x_b)]^{1/n}}{\exp(\ln\theta_b)} \tag{20}$$

Now, we have a complete system for obtaining the kinetic parameters of crystallization by using equation (11) and (17) to obtain the activation energy E, the reaction order *n* and equation (19) or (20) to obtain the frequency factor K_o, respectively.

4. Results and discussion

The validity of application and the full explanations of the this method, which can be described by equations (11), (17) and (19) or (20), have been thoroughly tested on computer simulated crystallization curves. These curves are calculated from equation (1) with perfectly known parameters include E, *n*, K_o at different heating rates.

As shown in Fig.1, the theoretical crystallized fraction curves *x*(t) are obtained at heating rates a=2, b=4, c=6, d=8 and e=10 K/min. The fraction curves *x*(t) are calculated according to equation (1) with n=2, E=130 (KJ/mol) and $K_o=1\times10^{14}(s^{-1})$

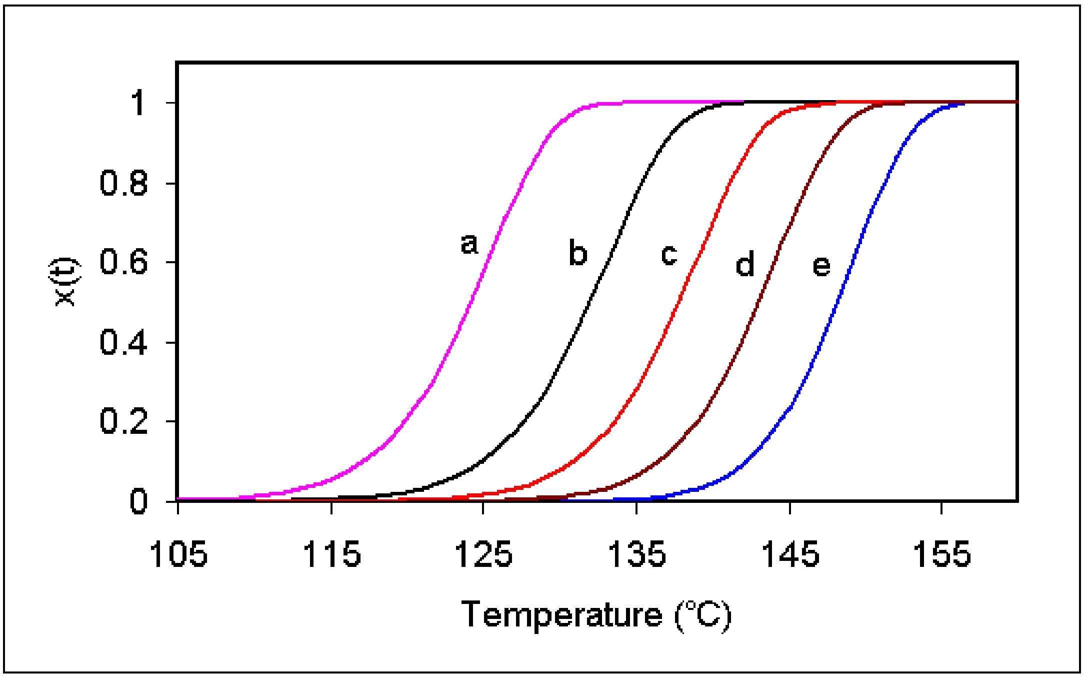

Fig. (1): Crystallized fraction $x_i(t)$*, calculated according to equation (11) with* $E=130.001$ *(KJ/mol),* $K_o=1\times10^{14}$ *(*s^{-1}*),* $n=2$ *and heating rates a=2, b=4, c=6, d=8 and e=10 K/min.*

Using two selected values of the crystallized fractions as, $x_1=0.3$ and $x_2=0.6$ at heating rates a=2, b=4, c=6, d=8 and e=10 (K/min), the corresponding data of the temperatures T_i(˚C) and times t_i (s) can be obtained and listed in tables (1) and (2), respectively. These data will be used to calculate E from the plot of ln(t) versus (1/T), by using equation (11). Thereafter, some of these data will be used to determine n and K_o, sequentially.

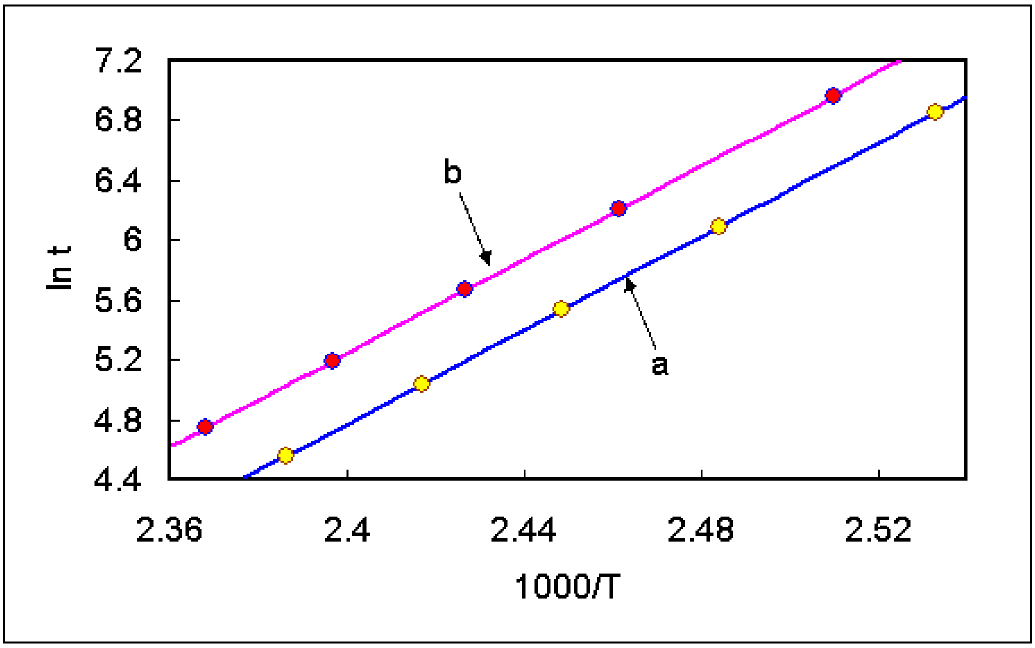

Fig. (2): The relation between ln(t) versus 1/T. Curve (a) at $x_1=0.3$ *and curve (b) at* $x_2=0.6$

The curve (a) of Fig.(2), shows the plot of ln(t_1) versus ($1/T_1$) of the data obtained in table (1) at x_1=0.3, giving rise to a straight line, from the slope (E/k) of which, according to equation (11), E can readily be evaluated by using the least square method. Therefore, the slope of curve (a) gives E =129.998 (KJ/mol). Also, the curve (b) of Fig. (2), gives the data listed in table (2) at x_2=0.6 which giving rise to a straight line, the activation energy E of which equal to 130.004 (KJ/mol). The average value of E obtained by using the results at x_1=0.3 and x_2=0.6 is found equal to 130.001 (kJ/mol).

Table (1): The temperature T_1(˚C) and time t_1(s) data obtained at x_1=0.3 from the crystallized fraction curves at 2, 4,6,8 and 10 K/min.

B (K/min.)	x_1	T_1(˚C)	t_1(s)
2	0.29999	121.6160	948.480
4	0.30000	129.4000	441.000
6	0.29999	135.2596	252.596
8	0.30000	140.5820	154.365
10	0.29999	145.9110	95.466

Table (2): The temperature T_2(˚C) and time t_2(s) data obtained at x_2=0.6 from the crystallized fraction curves at 2, 4,6,8 and 10 K/min.

B (K/min.)	x_2	T_2(˚C)	t_2(s)
2	0.60005	125.2640	1057.920
4	0.60002	133.0960	496.440
6	0.60001	138.8914	288.914
8	0.59999	144.0644	180.483
10	0.60000	149.1521	114.912

It is worthwhile noting that, as shown in tables (1) and (2) and for the sake of simplicity, we have selected two values of x_1 and x_2 at 0.3 and 0.6 to obtain E. However, any other value of x(t) in the range 0.2< x(t) <0.8 of figure (fg1) may be used to obtain E with the same degree of accuracy. On the other hand, the aim of using two different values of x(t), as shown in Fig. (2), because the calculation of the kinetic exponent n requires the data obtained at two different values of x_a and x_b as seen below. Subsequently, the value of E=130.001 (KJ/mol) will be used now to obtain n and K_o according to equation (17) and equation (19) or (20), respectively.

Next, the value of n is obtained by using the parameters involved in equation (17). As shown in tables (1) and (2), the average values of x_a=0.29999 and x_b=0.60001. The measured values of intercept (ln θ_a) of curve (a) at x_1=0.3 and the intercept (ln θ_b) of curve (b) at x_2=0.6 are -32.751103 and -32.2810085, respectively (Fig.2). Making use of these values of the parameters involved in equation (17), the value of n is found equal to (2.007). It is worthwhile noting that the resulting values of n are independent on the value of E. Finally, the frequency factor K_o can be obtained after substituting by the value of n in equation (19) or (20). In the case of obtaining K_o by using equation (19), the values of n = 2.007, x_a=0.29999 and ln θ_a = -32.751103, and the value of K_o by using equation (19) is found equal to $1.00128x10^{14}$ s^{-1}. In conclusion, the values of E, n and Ko are found equal to 130.001 (KJ/mol), 2.007 and $1.00128x10^{14}$ s^{-1}, respectively.

We thus found the calculated kinetic parameters by using the complete system with different heating rates which satisfactorily agree with the predetermined ones. This gives us the confidence of the different heating rates technique as a method for obtaining the crystallization kinetic parameters. This fact confirms the reliability and accuracy of the theoretical model developed.

The method describing above gives values for the kinetic parameters of the crystallization reactions, which must be considered more accurate, as they are numerically adjusted in a deterministic way, for all possible values of the crystallized fraction thus including all the experimental data given by the DSC curves.

5. Conclusions

The crystallization kinetics process in the glassy systems is well understood when the most important parameters of crystallization kinetic are determined These parameters include the crystallization activation energy E(kJ/mol), the reaction order of crystallization n, and the frequency factor K_o(s^{-1}). In the present work, for the systems which obey the Johnson-Mehl-Avrami (JMA) theoretical model during crystallization, a complete system with different heating rates technique is applied successfully for calculating, in sequence, the kinetic parameters of crystallization of glassy system under non-isothermal conditions. First. the value of E(kJ/mol) is determined is by using the values of the temperature T_i (K) and time t_i (s) at the same values of the fraction of crystallization x(t) at different heating rates. Next, the kinetic exponent or the reaction order of crystallization n and the frequency factor K_o (s^{-1}) can be determined from the intercept of the straight line relation between (ln t_i) versus ($1/T_i$). Therefore, this technique, with different heating rates, can evaluated all parameters without include any approximations as that found in some of the other methods.

References

[1] S.A. Khan, M. Zulfequar, M. Husain, solid state communications 123, 463(2002).
[2] J. Holubova, Z. Cernosek and E. Cernoskova, J. Thermal analysis and Calorimetry, 62, 715 (2000)
[3] M.F. Kotkata, M.H. El-Fouly, M.B. El-Den, Latin American J. of Metallurgy and Materials, 5, 28(1985).
[4] J.A. Augis, J.E. Bennet, J. Thermal analysis 13, 283 (1978)

[5] Y.Q. Gao, W. Wang, F.Q. Zheng, X. Liu, J. Non-Cryst. Solids 81,135 (1986)
[6] Y.Q. Gao, W. Wang, J. Non-Cryst. Solids 81 (1986) 129-134.
[7] S. Mahadevan, A. Giridhar, A.K. Singh, J. Non-Cryst. Solids 88,11 (1986)
[8] F. Liu, F. Sommer, E.J. Mittemeijer, J. Mater. Res. 19,2586 (2004)
[9] A.S. Soltan, Physica B 307, 78 (2001)
[10] A.H. Moharram, A.A. Abu-sehly, M. Abu El-Oyoun, A.S. Soltan, Physica B 324,344 (2002).
[11] C.M. Lee, Y.I. Lin, T.S. Chin, J. Mater. Res. 19, 2929 (2004)
[12] M.S. Rasheedy, Phys. Stat. Solidi (a) 202, 1896 (2005)
[13] H. Yinnon, D.R. Uhlmann, J. Non-Cryst. Solids 54, 253 (1983)
[14] J. W. Christian, The Theory of Transformation in Metals and Alloys, 2nd Ed., Pergamon Press,1975.
[15] D.W. Henderson, J. Thermal Anal., 15, 325 (1979)
[16] J. Malek, Thermochim. Acta, 200, 325 (1992)
[17] W.A. Johnson and R.F. Mehl, Trans. Am. Ins. Min. (Metal) Engs., 135,416 (1939)
[18] M. Avrami, Kinetics of phase change. I General theory, J. Chem. Phys. 7, 1103 (1939)
[19] M. Avrami, Kinetics of phase change. II Transformation-time relations for random distribution of nuclei, J. Chem. Phys. 8, 212 (1940)
[20] M. Avrami, Granulation phase change, and microstructure; kinetics of phase change , J. Chem. Phys. 9, 177 (1941)
[21] D.W. Henderson, J. Non-Cryst. Solids 30, 301 (1979)

E-mail address: asasoltan2001@yahoo.com