ELSEVIER

Journal of Alloys and Compounds 270 (1998) 179–185

Journal of ALLOYS AND COMPOUNDS

A study on non-isothermal transformation kinetics. Application to the crystallization of $Sb_{0.20}As_{0.32}Se_{0.48}$ alloy

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Received 28 January 1998

Abstract

Non-isothermal differential scanning calorimetry is frequently employed to study the kinetics of transformation reactions and, in particular, the crystallization of glassy alloys. Such data are analyzed by the Kissinger method, which was originally derived for the study of homogeneous reactions. The consensus in the literature, over several decades, was that such applications (i.e. to heterogeneous solid state transformations) of the Kissinger method are not valid. In the present work the principal objections to these applications are addressed and alternative derivations of theoretical results are provided. These results demonstrate that the Kissinger method is valid for heterogeneous reactions of the type described by the Johnson–Mehl–Avrami equation in the isothermal case. Isothermal and non-isothermal data on the crystallization of $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy are presented. These experimental results and the discussion presented here help to clarify the effects of incubation time on the non-isothermal transformation kinetics and provide a further demonstration of the validity of the generalized Johnson–Mehl–Avrami theory for the description of heterogeneous solid state transformations. © 1998 Elsevier Science S.A.

Keywords: Glassy alloy; Heating rate; Isothermal and non-isothermal processes; Kinetic parameters; Preannealing

1. Introduction

The last decades have seen intense theoretical and practical interest in the application of isothermal and non-isothermal experimental analysis techniques to the study of phase transformations. While isothermal experimental analysis techniques are in most cases more definitive, non-isothermal thermoanalytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiments attractive. Non-isothermal experiments can be used to extend the temperature range of measurements beyond that accessible to isothermal experiments. Many phase transformations occur too rapidly to be measured under isothermal conditions because of transients inherently associated with the experimental apparatus. Industrial processes often depend on the kinetic behaviour of systems undergoing phase transformation under non-isothermal conditions. In this instance a definitive measurement of non-isothermal transformation kinetics is desirable.

The study of crystallization kinetics in glass-forming liquids has often been limited by the elaborate nature of the experimental procedures that are employed. The increasing use of thermoanalytical techniques such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) has, however, offered the promise of obtaining useful data with simple methods. A popular thermal analysis method developed by Kissinger [1,2] determines the kinetic parameters from graphs of the logarithm of the temperature squared, T_p, at the maximum of the reaction rate versus the reciprocal of T_p in non-isothermal experiments. This method was frequently used in studies of the crystallization of glassy alloys [3–6] despite the fact that the literature [7] on thermal analysis techniques reflected a consensus that application of the Kissinger method to solid state reactions is improper. However, the notable work of Henderson [8] has provided a theoretical basis for the treatment of non-isothermal analysis techniques and justifies the use of the Kissinger method for many solid state transformations. The three main objections to the use of this method for the study of solid state reactions were: (1) thermal gradients are inherent in non-isothermal methods. Thus, it was claimed that significant inaccuracy will result from the application of the Kissinger method which does not allow for the presence of temperature gradients. (2) The reaction rate

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0925-8388/98/$19.00
PII: S0925-8388(98)00352-1

equation which is appropriate for isothermal experiments is assumed in the Kissinger analysis. It is frequently argued that a term involving the temperature partial derivative must be included in the analysis of non-isothermal experiments; this point has been debated in the literature for several years. (3) The order of reaction equation assumed in the Kissinger analysis is appropriate for homogeneous transformations, (e.g., chemical reactions in a gas) but is not valid for the heterogeneous transformations which generally occur in solid state reactions.

Regarding the first objection, it is possible to describe simple procedures to reduce the influence of temperature gradients to negligible levels.

The confusion in the literature surrounding the proper form of the reaction rate equation in the Kissinger analysis (objection (2)) results from the assumption that the progress of a reaction can be described as a simple function of time and temperature. The volume fraction transformed is clearly a functional [9], dependent on the temperature history, and not a simple function. However, a result of the analysis presented in this paper and the principle assumption in Henderson's work [8] is that the reaction rate is an ordinary function of the temperature and the volume fraction transformed.

As for the third objection, Henderson [8] has shown that the Kissinger method can be applied to the analysis of many heterogeneous reactions. In the present work, an alternative treatment of non-isothermal transformation kinetics is provided. The quoted treatment indicates that the Kissinger method can be applied to any reaction of the type described by the Johnson–Mehl–Avrami (JMA) equation [10–13] in the isothermal case. The treatment presented here (as does that of Henderson) is as follows: (i) generalize the JMA approach to deal with non-isothermal heterogeneous reactions, and (ii) demonstrate that in the constant heating rate case (within negligible errors) the Kissinger relationship obtains.

Finally, isothermal and non-isothermal data on the crystallization of $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy are presented. Results on the influence of incubation time on non-isothermal experiments are included. The data are in good agreement with the theoretical results.

2. Theoretical background

In DSC the instrument supplies heat to either the sample being investigated or the reference material in order to keep their temperatures equal. The instantaneous heat supplied to the sample or reference is available as the output signal. The fraction of material transformed at any time is proportional to the amount of heat evolved. During crystallization of the glass an exothermic peak is observed because the enthalpy of the crystal is lower than that of the glass. The enthalpy corresponding to the area under the peak is equal to the heat of reaction.

2.1. Isothermal treatment

The Johnson–Mehl–Avrami equation [10–13] describes a wide variety of isothermal solid state transformations and has the form

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

where x is the volume fraction transformed after time t, n a dimensionless quantity called the kinetic exponent, and K the reaction rate constant, whose temperature dependence is generally expressed by the Arrhenius equation:

$$K(T) = K_0 \exp(-E/RT) \tag{2}$$

where K_0 is the frequency factor, T is the absolute temperature, and E is the activation energy for the transformation process with R the gas constant. Note that Eq. (1) describes isothermal processes so $K(T)$ is a constant, which depends on the temperature. An expression for the reaction rate, $\mathrm{d}x/\mathrm{d}t$, can be derived by differentiating Eq. (1) with respect to t, at constant temperature, giving

$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= nK^n t^{n-1}(1-x) \\ &= nK(1-x)[-\ln(1-x)]^{(n-1)/n} \end{aligned} \tag{3}$$

which is a simple function of the temperature and the volume fraction transformed.

When an isothermal experiment is performed using a DSC, the rates of crystallization at various times, $\mathrm{d}x/\mathrm{d}t$, are measured directly. However, the results can be more easily analyzed by Eq. (1). Taking twice the logarithm of Eq. (1) leads to the expression

$$\ln[-\ln(1-x)] = n \ln K + n \ln t \tag{4}$$

At a given temperature, values of n and K are determined from an isothermal DSC curve using Eq. (4) by least-squares fitting of $\ln[-\ln(1-x)]$ versus $\ln t$. Values of the $\ln K$ are evaluated at different temperatures by repeating the same procedure. The activation energy and frequency factor are then evaluated from the logarithmic form of Eq. (2) by least-squares fitting $\ln K$ versus $1/T$.

2.2. Non-isothermal treatment

A generalization of Eq. (1) to treat experiments in which temperature is a function of time is very interesting. If it is assumed that the transformation products and mechanism do not change with temperature, then it is reasonable to interpret Kt in Eq. (1) as being proportional to the number of atomic jumps within the interval t at temperature T. It is assumed that the progress of the transformation is determined by the number of atomic jumps in the general (non-isothermal) case as well, then Eq. (1) generalizes to

$$x(t)=1-\exp\left[-\left(\int_0^t K[T(t')]\mathrm{d}t'\right)^n\right]$$
$$=1-\exp(-I^n) \quad (5)$$

where $K[T(t')]$ is still given by Eq. (2) and $T(t')$ is the temperature at t'. Note that the volume fraction crystallized depends on t and the temperature history $T(t')$ for times t' earlier than t and the same is true for the integral I.

Deriving Eq. (5) with respect to time, the crystallization rate is obtained as

$$\mathrm{d}x/\mathrm{d}t=nK(1-x)I^{n-1} \quad (6)$$

The maximum crystallization rate is found for $\mathrm{d}^2x/\mathrm{d}t^2=0$, thus obtaining the relationship

$$nK_p(I^n)|_p=\beta EI_p/RT_p^2+(n-1)K_p \quad (7)$$

where $\beta=\mathrm{d}T/\mathrm{d}t$ is the heating rate for a non-isothermal process, and where the magnitude values which correspond to the maximum crystallization rate are denoted by subscript p.

By using the substitution $y'=E/RT'$ the integral I can be represented by the alternating series [14]

$$-e^{-y'}y'^{-2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{y'^k}$$

where it is possible to use only the first two terms, without making any appreciable error, and to obtain

$$I=RT^2K(\beta E)^{-1}\left(1-2\frac{RT}{E}\right) \quad (8)$$

if it is assumed that $T_0 \ll T$ (T_0 is the starting temperature), so that y_0 can be taken as infinite.

Substituting the last expression for I into Eq. (7), one obtains the relationship

$$I_p=(1-2RT_p/nE)^{1/n}$$

When this relationship is equated to Eq. (8) this gives

$$RT_p^2(\beta E)^{-1}K_0\exp(-E/RT_p)=(1-2RT_p/nE)^{1/n}(1-2RT_p/E)^{-1} \quad (9)$$

or in a logarithmic form

$$\ln(T_p^2/\beta)+\ln K_0R/E-E/RT_p\approx(2RT_p/E)(1-1/n^2) \quad (10)$$

where the function $\ln(1-z)$ with $z=2RT_p/nE$ or $z=2RT_p/E$ is expanded as a series and only the first term has been taken.

Note that Eq. (10) reduces to the Kissinger expression for the $n=1$ case as one might have anticipated since this corresponds to the homogeneous reaction case. Moreover, for most crystallization reactions the right-hand side (RHS) of Eq. (10) is generally negligible in comparison to the individual terms on the left-hand side for common heating rates ($\leq 100\,\mathrm{K\,min^{-1}}$). Thus, it can be seen that the Kissinger method is appropriate for the analysis not only of homogeneous reactions, but also for the analysis of heterogeneous reactions which are described by the JMA equation in isothermal experiments. The approximation in Eq. (10) (RHS=0) implies

$$\mathrm{d}[\ln(\beta/T_p^2)]\mathrm{d}(1/T_p)=-E/R$$

where the quoted approximation might introduce a 3% error in the value of E/R in the worst cases. (Typically, $n>1$ and $E/RT_p>25$ which suggests that the error introduced in E/R by setting the RHS of Eq. (10) to zero is considerably less than 1%.) Eq. (10) also serves to determine the frequency factor, K_0, from the intercept of the $\ln(T_p^2/\beta)$ versus $1/T_p$ plot. Eq. (6), which describes the time dependence of the reaction rate, and Eq. (10), which allows for the simple extraction of the parameters K_0 and E by means of the Kissinger method, form the basis for the analysis of constant heating rate data.

Finally, it should be noted that Eq. (10) with RHS=0 is obtained by considering that the term $2RT/E$ in Eq. (8) is negligible in comparison to unity, since in most crystallization reactions $E/RT \gg 1$ (usually $E/RT \geq 25$) [15]. Bearing in mind this assumption, Eq. (8) for the maximum crystallization rate may be rewritten as

$$I_p=RT_p^2K_p(\beta E)^{-1}$$

which, when substituted into Eq. (7), gives $I_p=1$. Then Eq. (6) permits us to obtain

$$n=(\mathrm{d}x/\mathrm{d}t)_pRT_p^2(0.37\beta E)^{-1} \quad (11)$$

which makes it possible to calculate the kinetic exponent n.

3. Experimental procedures

High purity (99.999%) antimony, arsenic and selenium in appropriate atomic per cent proportions were weighed into a quartz glass ampoule (6 mm diameter). The ampoule (7 g total) was sealed at a pressure of 10^{-4} Torr ($10^{-2}\,\mathrm{N\,m^{-2}}$) and heated in a rotating furnace at around 950°C for 24 h, submitted to a longitudinal rotation of $1/3\,\mathrm{rev\,min^{-1}}$ in order to ensure homogeneity of the molten material. It was then immersed in a receptacle containing water in order to solidify the material quickly, avoiding crystallization of the compound. The amorphous nature of the material was checked through a diffractometric X-ray scan, in a Siemens D500 diffractometer. The thermal behaviour was investigated using a Perkin-Elmer DSC7 differential scanning calorimeter with an accuracy of ±0.1°C. Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and melting enthalpies of high-purity zinc and indium supplied with the instrument. Powdered samples weighing about 20 mg (particles size around

40 μm) were crimped in aluminium pans, an empty aluminium pan was used as reference, and a constant flow of nitrogen was maintained in order to drag the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC furnace.

Isothermal transformation kinetics data for $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy were obtained by monitoring the time dependence of the DSC output for a series of temperatures. The DSC output, Q_{DSC}, is assumed to be proportional to the reaction rate, dx/dt ($Q_{DSC}=C dx/dt$, C is a constant), so the volume fraction crystallized, $x(t)$, is given by $x(t)=A(t)/A$, where

$$A(t)=\int_0^t Q_{DSC}\,dt' = C[x(t)-x(0)]$$

and $A=A(\infty)$. The technique for extracting the time exponent n and $K(T)$ in an isothermal experiment described by Eq. (1) is to plot $\ln\{\ln[A/(A-A(t))]\}$ versus $\ln t$, so that n is the slope and $K(T)=t_0^{-1}$, where t_0 is the time in seconds when $\ln\{\ln[A/(A-A(t))]\}=0$.

Non-isothermal transformation kinetics data for the above-mentioned alloy were obtained by scanning of the samples at room temperature through their glass transition temperature, T_g, at different heating rates: 1, 2, 4, 8, 16, 32 and 64 K min^{-1}. A typical DSC trace of $Sb_{0.20}As_{0.32}Se_{0.48}$ chalcogenide glass obtained at a heating rate of 8 K min^{-1} (Fig. 1) shows three characteristic phenomena which are resolved in the temperature region studied. The first ($T=454.7$ K) corresponds to the glass transition temperature T_g, the second ($T=496.1$ K) to the extrapolated onset of the crystallization at temperature T_c, and the third ($T=508.7$ K) to the peak temperature of crystallization T_p of the above chalcogenide glass. This behaviour is typical for a glass–crystalline transformation. It should be noted that temperatures T_g, T_c and T_p increase with increasing heating rate, as often occurs in the literature [16].

4. Results and discussion

The isothermal DSC measurements exhibit “an incubation time”, t_{inc}, during which no observable transformation occurs. The temperature dependence of t_{inc} can be described as an activated process with an energy near that for the phase transformation; this is often observed in studies of crystallization [17].

The DSC traces for a series of temperatures were integrated to yield plots of $\ln[-\ln(1-A(t)/A)]$ versus $\ln(t-t_{inc})$ which are shown in Fig. 2. Reasonably good straight lines are obtained; the n values determined from Fig. 2 and given in Table 1 for different temperatures range from 1.62 to 1.73 with a mean value of 1.67. The deviation from linearity at long times may reflect breakdown of the theory for $x(t)$ at the end of the transformation.

The logarithm of the rate constant, K, obtained from Fig.

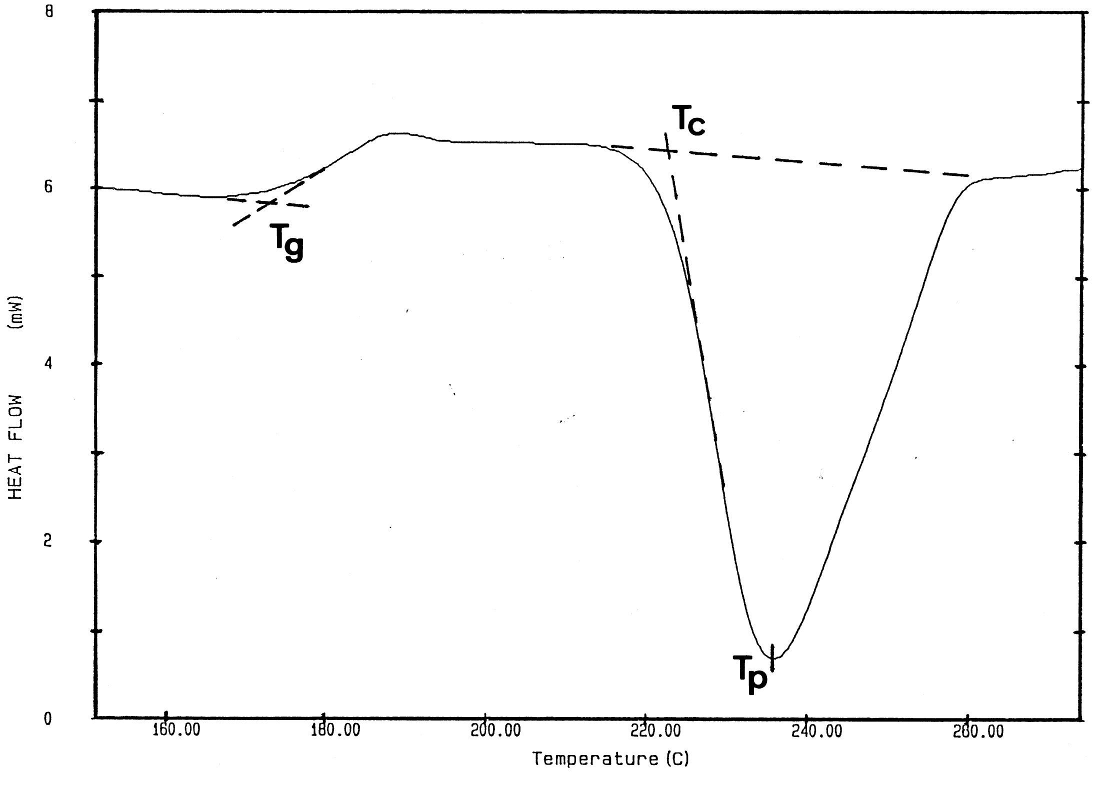

Fig. 1. Typical DSC trace for $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy at a heating rate of 8 K min^{-1}.

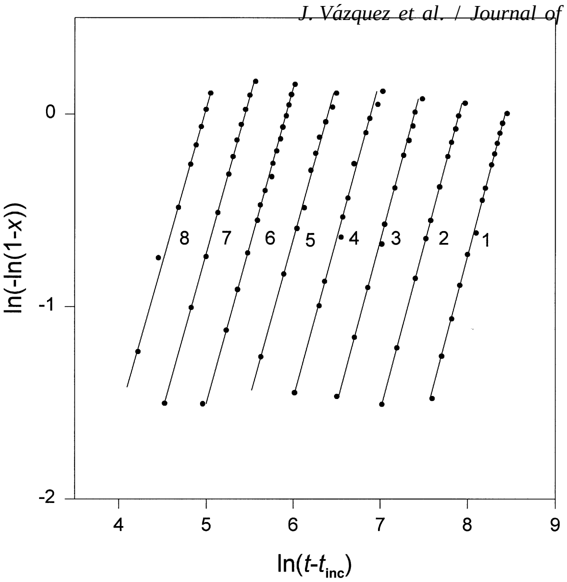

Fig. 2. Plots for extracting the JMA time exponent n in Eq. (1), as described in the text. Characteristic parameters are listed in Table 1 for the corresponding curve number.

2 is plotted versus $1/T$ in Fig. 3. The slope of the line, obtained from a least squares fit, gives $E=45.4$ kcal mol^{-1} for the activation energy and the intercept of the above line gives $K_0=4.22\times10^{17}$ s^{-1} for the frequency factor. There is little scatter about the lines in Figs. 2 and 3 despite the inherent experimental difficulties in establishing accurate base lines with this method.

The non-isothermal data for $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy, obtained at the heating rates given in Table 1, were analyzed using Eq. (10) with RHS$=0$ and Eq. (11) deduced in the preceding theory. A plot of $\ln(T_p^2/\beta)$ versus $1/T_p$ is shown in Fig. 4. A good straight line with little scatter results yielding $E=45$ kcal mol^{-1} for the activation energy and $K_0=1.88\times10^{17}$ s^{-1} for the frequency factor. The mean value of the kinetic exponent, according to Eq. (11), is $\langle n\rangle=1.69$.

Also shown in Fig. 4 are constant heating rate data obtained on a set of $Sb_{0.20}As_{0.32}Se_{0.48}$ samples which had previously been annealed through the incubation time (1100 s at 468 K) as determined in the isothermal experiments. It is possible to assume that this preanneal eliminates the effect of incubation in the constant heating rate experiments so as to permit direct comparisons with theory. (Recall that incubation is not described by the JMA theory, although the subsequent reaction is in the isothermal case.) The resulting values for E and K_0 are 46.1 kcal mol^{-1} and 7.69×10^{17} s^{-1}, respectively. These compare well with the above-mentioned isothermal values.

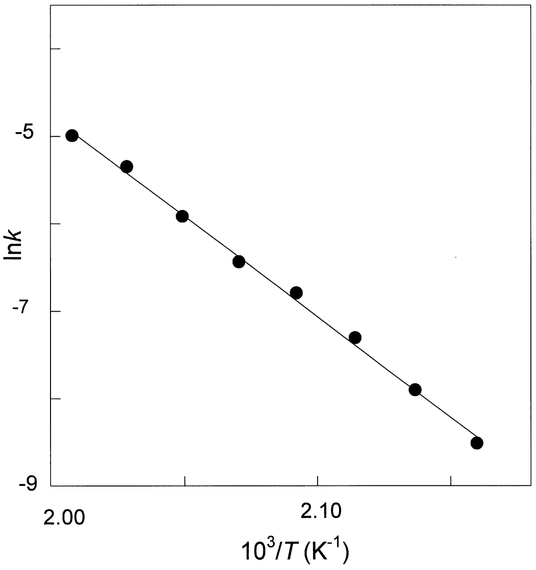

Fig. 3. Logarithm of the reaction rate constant, K, deduced from the isothermal measurements plotted versus T^{-1} (K is in s^{-1}).

As a further check on the adequacy of the generalized JMA equation for describing constant heating rate experiments, the DSC peak positions and shapes were computed from Eq. (6) using the values of E, K_0, and n determined from the isothermal measurements. Fig. 5 shows typical computed and experimental results obtained in constant heating rate experiments including the effect of preannealing through the incubation time. Generally, for preannealed samples the DSC peak positions are within 2 K of the predicted positions, the full width at half maximum (FWHM) is within 1 K, and the predicted asymmetry is observed. Unannealed samples exhibit narrower and less skewed DSC peaks than given by the generalized JMA

Table 1
Experimental and theoretical parameters for isothermal and constant heating rate experiments on $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy

Isothermal				Constant heating rate							
Run	T (K)	t_{inc} (s)	n	Run	β (K min^{-1})	T_p (K)			FWHM (K)		
						[Exp. (a)]	[Exp. (p)]	Theory	[Exp. (a)]	[Exp. (p)]	Theory
1	463	2322	1.73	1	1	491.1	478.7	477.0	17.6	18.0	18.2
2	468	1120	1.71	2	2	495.8	485.5	483.9	17.7	18.2	18.6
3	473	415	1.69	3	4	499.7	492.3	490.9	17.7	18.3	19.0
4	478	182	1.66	4	8	508.7	499.6	498.3	17.7	18.9	19.8
5	483	101	1.64	5	16	516.5	509.3	507.4	18.0	18.1	18.4
6	488	50	1.64	6	32	526.0	520.4	518.4	18.3	18.6	18.7
7	493	35	1.63	7	64	536.1	533.9	532.0	18.8	19.7	20.6
8	498	18	1.62								

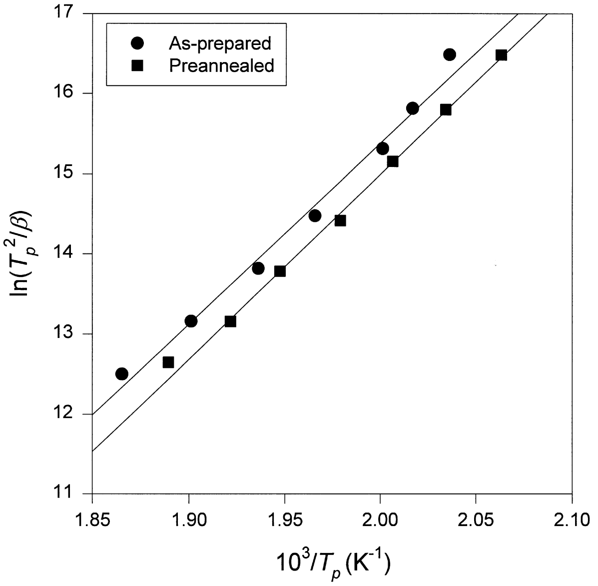

Fig. 4. Plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ and straight regression lines for as-prepared and preannealed samples.

theory. Table 1 summarizes the predicted and observed values of T_p and FWHM, both for as-prepared and preannealed experiments, at the heating rates employed in this study. It should be noted that the theoretical constant heating rate curves were based upon the best fit isothermal parameters and are skewed such that the right half maximum point lies approximately two-thirds as far from the maximum as the left half maximum point. This asymmetry is not seen with as-prepared samples [Exp. (a)] but is present in the preannealed samples [Exp. (p)].

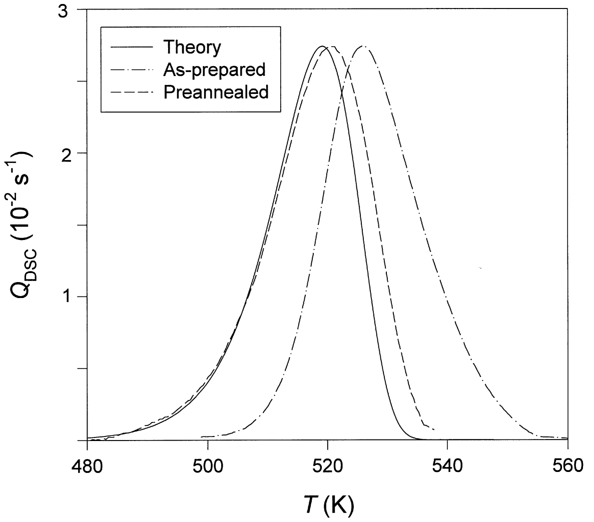

Fig. 5. Experimental and theoretical DSC traces for 32 K min^{-1} heating rate. Parameters used in the theoretical curve were obtained from isothermal data ($E = 45.4$ Kcal mol^{-1}; $K_0 = 4.22\times10^{17}$ s^{-1} and $\langle n\rangle = 1.67$). The area of the theoretical curve is normalized to unity. Peak heights of the experimental curves were scaled to match the theoretical curve. Experimental data are shown for as-prepared and preannealed samples.

5. Summary and conclusions

The JMA theory provides a satisfactory description of isothermal transformations as illustrated in Fig. 2. Thus, the JMA equation, Eq. (1) (rather than the order of reaction equation), was adopted as the basis for the study of non-isothermal transformations. A generalization appropriate for an arbitrary temperature–time history was required. As described earlier, the fraction transformed $x(t)$ must be a functional of the function $T(t')$ for all $t' < t$. An analogous case is found in Cahn's additivity criterion [18] for analyzing the progress of a reaction along an arbitrary path in a T-T-T diagram. The surprising result of this analysis, and that provided by Henderson [8], is that in the constant heating rate case, the descriptive equation, Eq. (10), is essentially independent of the kinetic exponent, n, and that the Kissinger equation holds. Thus, although the basic equation in Kissinger's analysis of homogeneous transformations is indeed inappropriate for heterogeneous solid state transformations, the Kissinger method can be applied to the analysis of heterogeneous transformations. Also, it is possible to understand why the Kissinger method had previously been successfully applied to the fitting of constant heating rate data in many studies of heterogeneous solid state reactions.

The validity of the theoretical description of the non-isothermal transformation case is indicated by the agreement observed in the kinetic parameters extracted from the isothermal and from the constant heating rate measurements in $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy. This agreement is particularly good for the samples in which the effects of incubation were removed by preannealing; the values for E and $\ln K_0$ agree within 2% which is within the limit of error inherent in the measurements. Another way of assessing the non-isothermal theory is to use the kinetic parameters deduced from isothermal studies to predict non-isothermal DSC curves. The close agreement between the observed and predicted DSC peak temperature, T_p, full width at half maximum, FWHM, and asymmetry support the correctness of the theoretical approach. It is possible to attribute the somewhat poorer results for the unannealed samples to the fact that the JMA equation does not describe incubation effects. An incubation time can be expected to inhibit transformation on the low temperature side of the reaction rate peak in a non-isothermal experiment resulting in a less skewed peak, as observed.

The principal results may be summarized as follows. (i) Henderson's assumption [8] that the JMA reaction rate equation holds for arbitrary temperature history and the assumption that the volume fraction crystallized is determined by the number of atom movements for arbitrary temperature history as described herein lead to equivalent theories and, in the non-isothermal case, indicate that the Kissinger method can be used to extract kinetic parameters. (ii) The results obtained for samples of $Sb_{0.20}As_{0.32}Se_{0.48}$ glassy alloy exhibiting incubation effects in the isothermal case are seen to be approximately described by the quoted theory. Moreover, it is shown that when incubation effects are eliminated, by preannealing, detailed agreement with theory is obtained. Thus, in the present work, for the preannealed samples, the DSC peak positions, FWHM, and asymmetry obtained in non-isothermal measurements are in remarkable agreement with theoretical predictions based upon kinetic parameters deduced from isothermal experiments. Also, the kinetic parameters deduced from non-isothermal experiments and those deduced from isothermal experiments agree within experimental uncertainties.

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