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An alternative treatment of non-isothermal heterogeneous transformations Application to the crystallization of $Ge_{0.13}Sb_{0.23}Se_{0.64}$ alloy

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Abstract

Continuous heating differential scanning calorimetry is frequently employed to study the kinetics of transformation reactions and, in particular, the crystallization of the glassy alloys. Such data are analyzed by the Kissinger method, which was originally derived for the study of homogeneous reactions. Although 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, nevertheless, by assuming that the transformation products and mechanism do not change with temperature, it is possible a valid application of Kissinger method to non-isothermal heterogeneous transformations. In this work, the principal objections to these applications are addressed and bearing in mind the quoted assumptions 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–Kolomogoroff equation in the isothermal case. Isothermal and continuous heating data on the crystallization of $Ge_{0.13}Sb_{0.23}Se_{0.64}$ semiconducting 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–Kolomogoroff theory for the description of heterogeneous solid state transformations.

Keywords: Glassy alloy; Heating rate; Isothermal and continuous heating processes; Kinetic parameters; Preannealing

1. Introduction

Amorphous materials themselves are nothing new. The iron-rich siliceous glasses found in the moon rocks, brought back by the Apollo missions, are billions of years old. Man has been making glasses (mainly silica) for centuries, as is proven by the colored glass used artistically in cathedrals and other buildings during the middle ages. What is relatively recent is the scientific study of amorphous solids, and interest in them grows daily as new glasses are obtained, some of which have a promising technological future. Proof of the growing interest in these solids is the number of scientific works published yearly on the subject, which has increased threefold since the seventies and is still growing. Glassy solids of great interest are the chalcogenide glasses, which are essentially compounds containing sulfur, selenium or tellurium. These materials have received much attention over a long period because of their glass-forming ability and interesting optical, electronic and acoustic properties. Therefore, the advances that have been made in physics and chemistry of the glassy materials during the last 40 years have been very appreciated within the research community. Among the different techniques used to the study of the quoted materials, the differential scanning calorimetry (DSC) has promoted an intense theoretical and practical interest. The quoted technique has been used extensively for the study of the kinetics of phase transformation processes and chemical reactions [1], both under isothermal and non-isothermal regime. While isothermal experimental analysis regime is in most cases, more definitive, non-isothermal thermoanalytical regimes have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiments attractive. 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 behavior 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

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of thermoanalytical techniques such as differential thermal analysis (DTA) or DSC has, however, offered the promise of obtaining useful data with simple methods. A widespread thermal analysis method developed by Kissinger [2,3] 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 [4–7] despite the fact that literature [8] 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 [9] 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 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 over 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 the time and temperature. The volume fraction transformed is clearly a functional [10], 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 [9] is that the reaction rate is an ordinary function of the temperature and the volume fraction transformed.

As for the third objection, Henderson [9] 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–Kolomogoroff (JMAK) equation [11–15] in the isothermal case. The treatment presented here (as does that of Henderson) goes as follows: (i) generalize the JMAK 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 $Ge_{0.13}Sb_{0.23}Se_{0.64}$ semiconducting 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 development

The theoretical basis for interpreting DTA or DSC results is provided by the formal theory of transformations kinetics as developed by JMAK [11–15]. A similar approach was also adopted by Erofeev and Mitzkevich [16]. In its basic form the theory describes the evolution with time, t, of the volume fraction crystallized, x, in terms of the nucleation frequency per unit volume, I_V and the crystal growth rate u, as

$$x(t) = 1 - \exp\left\{-g\int_0^t I_V(\tau)\left[\int_\tau^t u(t')\,\mathrm{d}t'\right]^m \mathrm{d}\tau\right\} \tag{1}$$

if the quoted rate is isotropic, an assumption which is in agreement with the experimental evidence, since in many transformations the reaction product grows approximately as spherical nodules [17]. At Eq. (1) m is an exponent, which depends on the dimensionality of the crystal growth and g is a geometric factor, which depends on the dimensionality and shape of crystal growth, and therefore its dimension equation can be expressed as [18]:

$$[g] = [L]^{3-m}, \quad [L]\ \text{is the length}$$

2.1. Isothermal regime

For the important case of isothermal crystallization with nucleation frequency and growth rate independent of time, Eq. (1) can be integrated, resulting in

$$\begin{aligned} x(t) &= 1 - \exp\left[-gI_V u^m \int_0^t (t-\tau)^m\,\mathrm{d}\tau\right] \\ &= 1 - \exp(-g' I_V u^m t^n) \end{aligned} \tag{2}$$

where $n = m + 1$ for $I_V \neq 0$ and g' a new shape factor.

By considering a sufficiently limited range of temperature (such as the range of crystallization peaks in DTA or DSC experiments) both I_V and u may be described in a zeroth-order approximation by

$$I_V \approx I_{V0} \exp\left(-\frac{E_N}{RT}\right) \tag{3}$$

and

$$u \approx u_0 \exp\left(-\frac{E_G}{RT}\right) \tag{4}$$

where E_N and E_G are the effective activation energies for nucleation and growth, respectively. Accordingly, Eq. (2) can be taken as a detailed specific case of the JMAK relationship:

$$x(t) = 1 - \exp\left[-(Kt)^n\right] \tag{5}$$

K being the effective overall reaction rate constant given by the expression:

$$K = K_0 \exp\left(-\frac{E}{RT}\right) \tag{6}$$

where $E = (E_N + mE_G)/n$ is the effective activation energy describing the overall crystallization process and K_0 the frequency factor. It should be noted that, according to Eqs. (2) and (5), K^n is proportional to $I_V u^m$.

On the other hand, the crystallization rate, dx/dt, is obtained by deriving Eq. (5) with respect to time, at constant temperature, giving

$$\frac{\mathrm{d}x}{\mathrm{d}t} = nK^n t^{n-1}(1-x) = nK(1-x)\left[-\ln(1-x)\right]^{(n-1)/n} \tag{7}$$

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, dx/dt, are measured directly. However, the results can be more easily analyzed by Eq. (5). Taking twice the logarithm of Eq. (5) leads to the expression:

$$\ln\left[-\ln(1-x)\right] = n \ln t + n \ln K \tag{8}$$

At a given temperature, values of n and K are determined from an isothermal DSC curve using Eq. (8) 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. (6) by least-squares fitting $\ln K$ versus $1/T$.

2.2. Non-isothermal regime

A generalization of Eq. (5) 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. (5) 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. (5) generalizes to

$$x(t) = 1 - \exp\left[-\left(\int_0^t K\left[T(t')\right]\mathrm{d}t'\right)^n\right] = 1 - \exp(-I^n) \tag{9}$$

where $K[T(t')]$ is still given by Eq. (6) 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.

Taking the derivative of Eq. (9) with respect to time, the crystallization rate is obtained as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = nK(1-x)I^{n-1} \tag{10}$$

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

$$nK_p(I^n)_p = \frac{\beta E I_p}{RT_p^2} + (n-1)K_p \tag{11}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate for a non-isothermal process, and where the quantity 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 sum of alternating series [19]:

$$S(y, y_0) = \left[(-\exp(-y'))y'^{-2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{y'^k}\right]_{y_0}^{y}$$

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

$$I = RT^2K(\beta E)^{-1}\left(1 - \frac{2RT}{E}\right) \tag{12}$$

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

Substituting the last expression for I into Eq. (11), one obtains the relationship:

$$I_p = \left(1 - \frac{2RT_p}{nE}\right)^{1/n}$$

When this relationship is equated to Eq. (12) this gives

$$RT_p^2(\beta E)^{-1}K_0\exp\left(-\frac{E}{RT_p}\right) = \left(1 - \frac{2RT_p}{nE}\right)^{1/n}\left(1 - \frac{2RT_p}{E}\right)^{-1} \tag{13}$$

or in a logarithmic form:

$$\ln\left(\frac{T_p^2}{\beta}\right) + \ln\left(\frac{K_0R}{E}\right) - \frac{E}{RT_p} \approx \left(\frac{2RT_p}{E}\right)\left(1 - \frac{1}{n^2}\right) \tag{14}$$

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.

It should be noted that Eq. (14) 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. (14) 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 JMAK equation in isothermal experiments. The approximation in Eq. (14) (RHS = 0) implies

$$\frac{\mathrm{d}[\ln(T_\mathrm{p}^2/\beta)]}{\mathrm{d}(1/T_\mathrm{p})} = \frac{E}{R}$$

where the quoted approximation might introduce a 3% error in the value of E/R in the worst cases. (typically, $n > 1$ and $E/RT_\mathrm{p} > 25$ which suggests that the error introduced in E/R by setting the RHS of Eq. (14) to zero is considerably less than 1%). Eq. (14) also serves to determine the frequency factor, K_0, from the intercept of the $\ln(T_\mathrm{p}^2/\beta)$ versus $1/T_\mathrm{p}$ plot. Eq. (10), which describes the time dependence of the reaction rate, and Eq. (14), 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. (14) with RHS = 0 is obtained by considering that the term $2RT/E$ in Eq. (12) is negligible in comparison to unity, since in most crystallization reactions $E/RT \gg 1$ (usually $E/RT \geq 25$) [20]. Bearing in mind this assumption, Eq. (12) for the maximum crystallization rate may be rewritten as

$$I_\mathrm{p} = RT_\mathrm{p}^2 K_\mathrm{p}(\beta E)^{-1}$$

which, when substituted into Eq. (11), gives $I_\mathrm{p} = 1$. Then Eq. (10) permits us to obtain

$$n = \left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_\mathrm{p} RT_\mathrm{p}^2 (0.37\beta E)^{-1} \qquad (15)$$

which makes it possible to calculate the kinetic exponent n.

3. Experimental details

The semiconducting $\mathrm{Ge_{0.13}Sb_{0.23}Se_{0.64}}$ glassy was made from their components of 99.999% purity, which were pulverized to less than 64 μm, mixed in adequate proportions, and introduced into a quartz ampoule. The ampoule (7 g per batch) was sealed at a pressure of 10^{-2} Pa and put into a furnace at 1223 K for 72 h, turning at 1/3 rpm, to improve homogeneity of the molten material, and then the ampoule was quenched in water with ice to avoid the crystallization. The capsule containing the sample was then put into a mixture of hydrofluoridic acid and hydrogen peroxide to corrode the quartz and make it easier to extract the alloy. The amorphous state of the material was confirmed by a diffractometric X-ray scan, in a Siemens D500 diffractometer, showing an absence of the peaks, which are characteristic of crystalline phases. The homogeneity and composition of the sample were verified through scanning electron microscopy (SEM) in a JEOL, scanning microscope JSM-820. The thermal behavior was investigated using a Perkin-Elmer DSC7 differential scanning calorimeter with an accuracy of ±0.1 K.

Isothermal transformation kinetic data for $\mathrm{Ge_{0.13}Sb_{0.23}Se_{0.64}}$ glassy alloy were obtained by monitoring the time dependence of DSC output for a series of temperatures. The DSC output, Q_DSC, is assumed to be proportional to the reaction rate, $\mathrm{d}x/\mathrm{d}t$ ($Q_\mathrm{DSC} = C\,\mathrm{d}x/\mathrm{d}t$, C is a constant), so the volume fraction crystallized, $x(t)$, is given by $x(t) = A(t)/A$, where

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

and $A = A(\infty)$. The technique for extracting the time exponent n and $K(T)$ in an isothermal experiment described by Eq. (5) 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 kinetic 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: 2, 4, 8, 16, 32 and 64 $\mathrm{K\,min^{-1}}$. A typical thermogram of $\mathrm{Ge_{0.13}Sb_{0.23}Se_{0.64}}$ chalcogenide glass obtained at a heating rate of 32 $\mathrm{K\,min^{-1}}$ (Fig. 1) shows three characteristic phenomena, which are resolved in the temperature region studied. The first (T = 493.3 K) correspond to the glass transition temperature, T_g, the second (T = 601.6 K) to the extrapolated onset of the crystallization at temperature, T_c, and the third (T = 618.3 K) to the peak temperature of crystallization, T_p, of the above chalcogenide glass. This behavior is typical for a glass-crystal 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 [21].

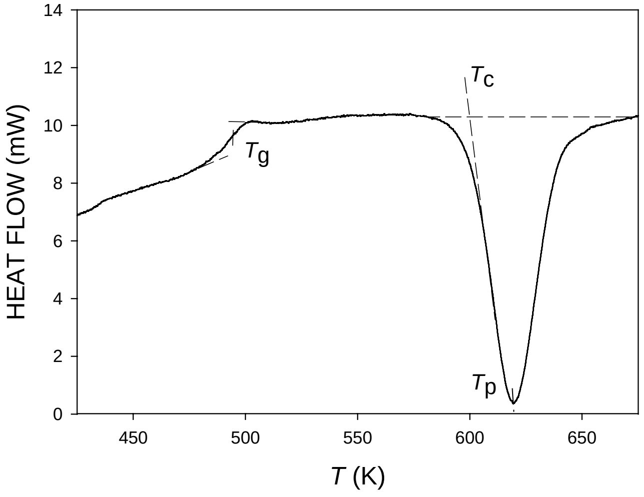

Fig. 1. Typical thermogram for $\mathrm{Ge_{0.13}Sb_{0.23}Se_{0.64}}$ glassy alloy at a heating rate of 32 $\mathrm{K\,min^{-1}}$.

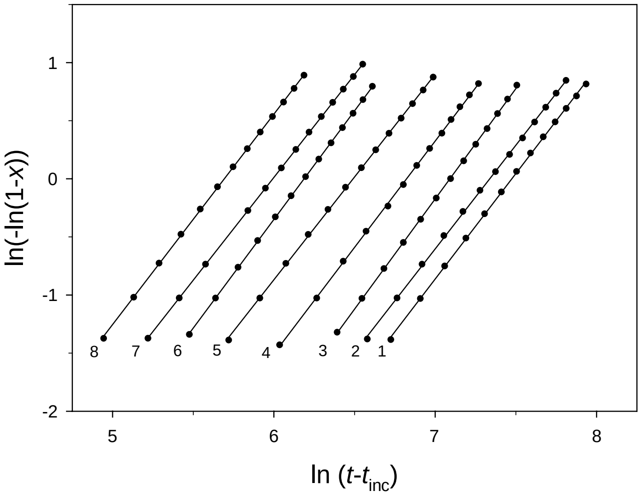

Fig. 2. Plots for extracting the kinetic exponent, *n*, in Eq. (5), as described in the text. Characteristic parameters are listed in Table 1 for the corresponding curve number.

4. Results and discussion

The isothermal thermograms 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 [22].

The DSC traces for a series of temperatures were integrated to yield plots of $\ln[-\ln(1-A(t)/A)]$ versus $\ln(t-t_{\mathrm{inc}})$ 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 1.77 to 1.90 with a mean value of 1.82. 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. 2 is plotted versus $1/T$ in Fig. 3. The slope of the line, obtained from a least-squares fit, gives $E = 56.8\,\mathrm{kcal\,mol^{-1}}$ for the activation energy and the intercept of the above line gives $K_0 = 4.85\times10^{18}\,\mathrm{s^{-1}}$ 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.

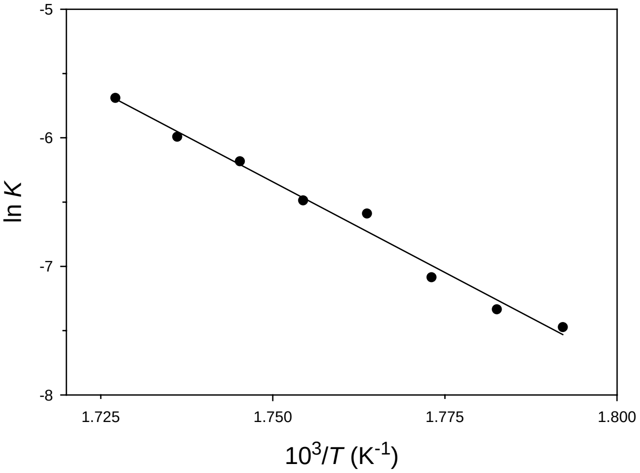

Fig. 3. Logarithm of the reaction rate constant, K, deduced from the isothermal measurements plotted vs. $1/T$ (K is in $\mathrm{s^{-1}}$).

With the aim of correctly analyzing the non-isothermal crystallization of the $Ge_{0.13}Sb_{0.23}Se_{0.64}$ semiconducting alloy it is assumed that the nucleation process takes place early in the transformation and the nucleation rate is zero thereafter, known case as “site saturation”. Moreover, it is considered that the transformation products and mechanism for the crystallization of the above-mentioned alloy do not change with temperature. Thus, the non-isothermal crystallization data for the quoted alloy, obtained at the heating rates given in Table 1, were analyzed using Eq. (14) with RHS = 0 and Eq. (15) 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 $E = 47.7\,\mathrm{kcal\,mol^{-1}}$ for the activation energy and $K_0 = 1.80\times10^{15}\,\mathrm{s^{-1}}$ for the frequency factor. The mean value of the kinetic exponent, according to Eq. (15), is $\langle n\rangle = 1.96$.

Also shown in Fig. 4 are constant heating rate data obtained on a set of $Ge_{0.13}Sb_{0.23}Se_{0.64}$ samples which had

Table 1
Experimental and theoretical parameters for isothermal and constant heating rate experiments on $Ge_{0.13}Sb_{0.23}Se_{0.64}$ glassy alloy

Isothermal				Constant heating rate							
Run	T (K)	t_{inc} (s)	n	Run	β ($\mathrm{K\,min^{-1}}$)	T_p (K)			FWHM (K)		
						[Exp. (a)]	[Exp. (p)]	Theory	[Exp. (a)]	[Exp. (p)]	Theory
1	558	1578	1.82	1	2	581.1	577.2	576.8	14.2	14.9	15.4
2	561	1235	1.78	2	4	588.0	584.1	583.6	14.6	15.3	15.9
3	564	976	1.90	3	8	597.5	593.6	593.1	15.0	15.7	16.3
4	567	771	1.83	4	16	607.7	603.7	603.2	15.3	16.2	16.7
5	570	609	1.77	5	32	618.3	614.2	613.7	15.9	16.8	17.3
6	573	424	1.87	6	64	631.3	627.7	626.6	16.3	17.3	17.8
7	576	296	1.77								
8	579	206	1.81								

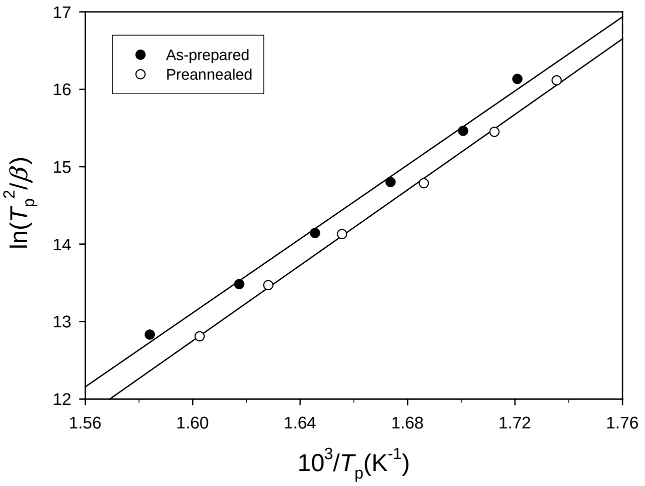

Fig. 4. Plots of $\ln(T_p^2/\beta)$ vs. $1/T_p$ and straight regression lines for as-prepared and preannealed samples.

previously been annealed through the incubation time (980 s at 564 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 JMAK theory, although the subsequent reaction is in the isothermal case.) The resulting values for E and K_0 are 48.7 kcal mol^{-1} and 6.03×10^{15} s^{-1}, respectively.

As a further check on the adequacy of the generalized JMAK equation for describing constant heating rate experiments, the DSC peak positions and shapes were computed from Eq. (10) using the values of E, K_0, and n determined from the isothermal measurements. Fig. 5 shows typical computed and experimental results obtained in continuous heating experiments including the effect of preannealing through the incubation time. Generally, for preannealed samples the DSC peak positions are within 1 K of the predicted positions, the full width at half maximum (FWHM) is also within 1 K, and the predicted asymmetry is observed. Unannealed samples exhibit narrower and less skewed DSC peaks than given by the generalized JMAK 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 continuous heating 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)].

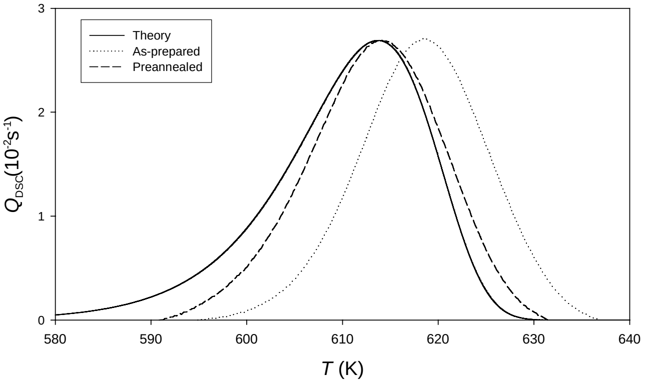

Fig. 5. Experimental and theoretical DSC traces for 32 K min^{-1} heating rate. Parameters used in the theoretical curve were obtained from isothermal data ($E = 56.8$ kcal mol^{-1}, $K_0 = 4.85 \times 10^{18}$ s^{-1} and $\langle n \rangle = 1.82$). The area of the theoretical curve is normalized to unity. Peak heights of the experimental curves were scaled to match the theoretical curve. Experimental data are shown for as-prepared and preannealed samples.

The JMAK theory provides a satisfactory description of isothermal transformations as illustrated in Fig. 2. Thus, the JMAK equation (Eq. (5)) (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 [23] 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 [9], is that in the continuous heating case, the descriptive equation, Eq. (14), 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 continuous heating 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 continuous heating measurements in $Ge_{0.13}Sb_{0.23}Se_{0.64}$ 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 3% 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 JMAK 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.

5. Conclusions

A theoretical method has been developed to generalize the JMAK equation in the case of the non-isothermal transformations. This method assumes that the transformation products and mechanism do not change with temperature. In this sense the principal results may be summarized as follows. (i) Henderson's assumption [9] that the JMAK 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 the $Ge_{0.13}Sb_{0.23}Se_{0.64}$ 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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