Journal of Thermal Analysis, Vol. 13 (1978) 283–292

CALCULATION OF THE AVRAMI PARAMETERS FOR HETEROGENEOUS SOLID STATE REACTIONS USING A MODIFICATION OF THE KISSINGER METHOD

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(Received June 13, 1977)

Several isothermal experiments are generally needed to determine the parameters of the Avrami equation which describe most of the heterogeneous solid state reactions. Differential scanning calorimeters are suitable for such experiments. While most differential thermal analysis (DTA) apparatus cover a wider temperature range than DSC apparatus they cannot be used to perform isothermal determinations. However, Kissinger has already shown how activation energy and frequency factor can be calculated from DTA experiments for the case of homogeneous reactions following first order kinetics. We derive in this paper an extension of the Kissinger method and show its applicability to heterogeneous reactions described by an Avrami expression. The new method will allow the study of the kinetics of metallic reactions at the higher temperature range obtainable with DTA. The transformation kinetics of the metastable equiatomic tin-nickel alloy are given as an example.

Most reactions in solid metallic phases are empirically described by the Avrami equation [1] where x is the amount of material transformed at the time t,

$$x = 1 - \exp\left[-(kt)^n\right]. \tag{1}$$

n is a dimensionless exponent, k has the dimension of reaction rate and is given by an Arrhenius type of relation

$$k = \nu \exp - \frac{\Delta E}{RT} \tag{2}$$

where

ν = frequency factor
ΔE = activation energy
R = gas constant
T = Kelvin temperature

The transformation can be completely described in time, temperature and transformed fraction co-ordinates if n, ΔE, and ν are known. The easiest way to calculate these three parameters is to run isothermal experiments to determine the change of x with time. The data is generally reduced [2] by fitting the equation:

$$\ln \frac{1}{1-x} = (kt)^n. \tag{3}$$

While isothermal experiments can conveniently be performed in a differential scanning calorimeter (DSC), the maximum operable temperature is 750° which presents quite a limitation for the study of metallic solid state reactions. Another available method has been differential thermal analysis (DTA) which can be operated at much higher temperatures. Unfortunately DTA is essentially a dynamic technique wherein time and temperature variables are intermixed and therefore no true isothermal experiment can be conducted in a DTA setup. Kissinger [3], in his study of homogeneous reactions which follow the first order rate equation:

$$\dot{x} = k(1 - x) \tag{4}$$

developed a method where both ΔE and ν can be determined from DTA experiments run at different heating rates. In the course of studying the kinetics of the transformation of tin-nickel [4], which occurs in the working range of both the DSC and DTA, we have been able to extend the Kissinger method to solid state reactions obeying an Avrami law.

Theory

During a DTA experiment the temperature of the furnace is changed linearly with time at a given rate α (degrees per second). The furnace temperature in Kelvin is:

$$T = T_0 + \alpha t \tag{5}$$

where T_0 is the initial temperature.

Assuming that the dynamic case is a close succession of isothermal ones, we can keep the Avrami expression for the fraction of transformed material:

$$x = 1 - \exp\left[-(kt)^n\right].$$

Because of Eq. (5) the rate constant varies with time and kt is no longer linear in t but a more complicated function such as:

$$kt = u = \nu t \exp\left[-\frac{\Delta E}{R(T_0 + \alpha t)}\right] \tag{6}$$

and Eq. (1) becomes

$$x = 1 - \exp(-u^n). \tag{7}$$

The successive time derivations of x are

$$\dot{x} = \dot{u}\, n\, u^{n-1}(1 - x) \tag{8}$$

and

$$\ddot{x} = [\ddot{u}\, u - \dot{u}^2(n\, u^n - n + 1)]n\, u^{n-2}(1 - x) \tag{9}$$

Assuming that the maximum rate of reaction coincides with the DTA peak, its position is given by

$$\ddot{u}\,u - \dot{u}^2[n\,u^n - n + 1] = 0 \tag{10}$$

Since we have $T = T_0 + \alpha t$ and simplifying

$$\dot{u} = v \exp\left(-\frac{\Delta E}{RT}\right) + vt\frac{\Delta E\alpha}{RT^2}\exp\left(-\frac{\Delta E}{RT}\right)$$

or

$$\dot{u} = \frac{u}{t} + au = u\left(\frac{1}{t} + a\right)$$

where

$$a = \frac{\Delta E\alpha}{RT^2},$$

and

$$\ddot{u} = \frac{\dot{u}}{t} - \frac{u}{t^2} + a\dot{u}$$

or

$$\ddot{u} = \dot{u}\left(\frac{1}{t} + a\right) - \frac{u}{t^2} = u\left[\left(\frac{1}{t} + a\right)^2 - \frac{1}{t^2}\right].$$

Equation (10) becomes

$$u^2\left[\left(\frac{1}{t} + a\right)^2 - \frac{1}{t^2}\right] - u^2\left[\left(\frac{1}{t} + a\right)^2\right][n\,u^n - n + 1] = 0$$

and is satisfied if

$$nu^n - n + 1 = 1 - \frac{1}{(1 + at)^2}. \tag{11}$$

Putting back the original expression for u, i.e., Eq. (6) we have

$$v^n \exp\left(n\frac{\Delta E}{RT_M}\right) = \left(\frac{T_M - T_0}{\alpha}\right)^{-n}\left[1 - \frac{1}{n\left(1 + \frac{\Delta E}{R}\frac{T_M - T_0}{T_M^2}\right)^2}\right] \tag{12}$$

where T_M corresponds to the temperature of the maximum of the DTA curve. Equation (12) can be solved graphically for $\frac{\Delta E}{R}$ if v is assumed or known. While the left side is a steeply decreasing function of $\frac{\Delta E}{R}$, the right side is approximately constant. The value of $\frac{\Delta E}{R}$ which satisfies both sides is given by the intersection of the corresponding curves and this value is the activation energy for the observed T_M.

The result of Eq. (12) can be applied to the self-consistent study of solid-state reactions by DTA without the prior knowledge of the frequency factor. DTA has been used to investigate kinetics of reactions in homogeneous systems by the Kissinger method. The fundamental expression of Kissinger's method is:

$$\nu \exp\left(-\frac{\Delta E}{RT_{\mathrm{M}}}\right) = \frac{\Delta E\alpha}{RT_{M}^{2}}\,. \tag{13}$$

Equation (13) was derived by starting with the first order rate Eq. (4) which corresponds to a special case of the Avrami equation where $n = 1$. Thus (13) can only be used for solid state reactions where $n = 1$ and unfortunately this is not often the case. Our treatment utilizes the first and second derivatives of a general Avrami equation and is valid for any value of n and therefore should be more applicable to solid-state reactions.

For most solid-state reactions one typically observes that, $\Delta E > 10$ Kcal/mol [0.43 eV] and $T_{\mathrm{M}} < 3000$ K.
So

$$\frac{\Delta E}{R}\,\frac{T_{\mathrm{M}} - T_0}{T_{\mathrm{M}}^2} \gg 1$$

and (12) becomes:

$$\nu^{n} \exp\left(-n\frac{\Delta E}{RT_{\mathrm{M}}}\right) \simeq \left(\frac{T_{\mathrm{M}} - T_0}{\alpha}\right)^{-n}. \tag{14}$$

Equation (14) written for $n = 1$ is:

$$\nu \exp\left(-\frac{\Delta E}{RT_{\mathrm{M}}}\right) \simeq \left(\frac{T_{\mathrm{M}} - T_0}{\alpha}\right)^{-1}. \tag{15}$$

Equation (15) is significantly different from Kissinger's result (13) and it occurs that the Kissinger method is only valid for the limiting case where:

$$\frac{\Delta E}{R}\,\frac{T_{\mathrm{M}} - T_0}{T_{\mathrm{M}}^2} \ll 1\,.$$

However, if both Eqs (13) and (15) are used to plot $\ln \frac{\alpha}{T_{\mathrm{M}}^2}$ versus $\frac{1}{T_{\mathrm{M}\alpha}}$ as in the Kissinger case and

$$\ln \frac{\alpha}{T_{\mathrm{M}} - T_0} \text{ versus } \frac{1}{T_{\mathrm{M}\alpha}} \text{ as in the present case,}$$

for various heating rates, they will generally lead to two straight lines of practically equal slope $\frac{\Delta E}{R}$, since over a small temperature range a constant β can always be found such that:

$$T_{\mathrm{M}}^2 \simeq \beta(T_{\mathrm{M}\alpha} - T_0)\,.$$

Recognizing that the right side of expression (14) is the time required to reach T_M (since $T_M = T_0 + \alpha t_m$), the equation reduces to

$$kt \approx 1$$

which means that, as should be expected, the peak of the DTA curve occurs when the argument of the exponential in the Avrami equation is close to unity.

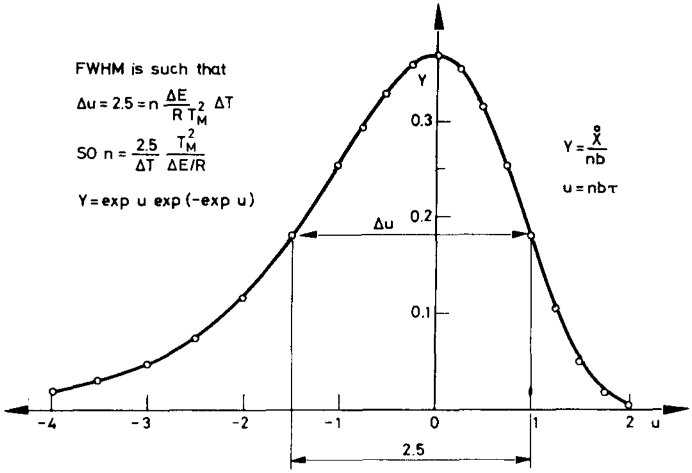

Fig. 1. Plot of Eq. (16) in reduced variables, basis of the determination of the exponent n

Consequently we believe that Eq. (12), or its approximation (14), justifies our modification of the Kissinger method $\left(\text{i.e., use of } \frac{\alpha}{T_m - T_0} \text{ instead of } \frac{\alpha}{T_M^2}\right)$ which thus can be used for kinetics described by an Avrami equation regardless of the value of the exponent n and will give an accurate estimate of $\frac{\Delta E}{R}$.

It also follows that reactions having the same $\frac{\Delta E}{R}$ but different Avrami exponent n will show a DTA peak at the same temperature. However, the value of n determines the shape of the peak and the higher n is, then the narrower is the peak. By a Taylor series expansion of Eq. (8) for values of u close to unity i.e., near T_M, we obtain the following approximate equation which describes the shape of the DTA peak:

$$\dot{x} = nb \exp(nb\tau) \exp[-\exp(nb\tau)] \qquad (16)$$

with

$$b = \frac{\Delta E}{RT^2}$$

and where τ is the temperature excursion measured from T_M. This curve in reduced variables, $u = nb\tau$ and $y = \dot{x}/nb$, is shown in Fig. 1. If $\Delta\tau_{FWHM}$ is the full width at half maximum of the DTA peak, then one can estimate n from the relation:

$$n = \frac{2.5}{\Delta\tau_{FWHM}} \frac{T_M^2}{\frac{\Delta E}{R}}. \tag{17}$$

Example of application

Transformation of the tin-nickel equiatomic alloy

The electrodeposited equiatomic alloy (65 weight per cent Sn — 35 weight per cent Ni) is not an equilibrium phase of the nickel-tin binary system and can only be prepared by electroplating [5], or from more recent results by sputtering

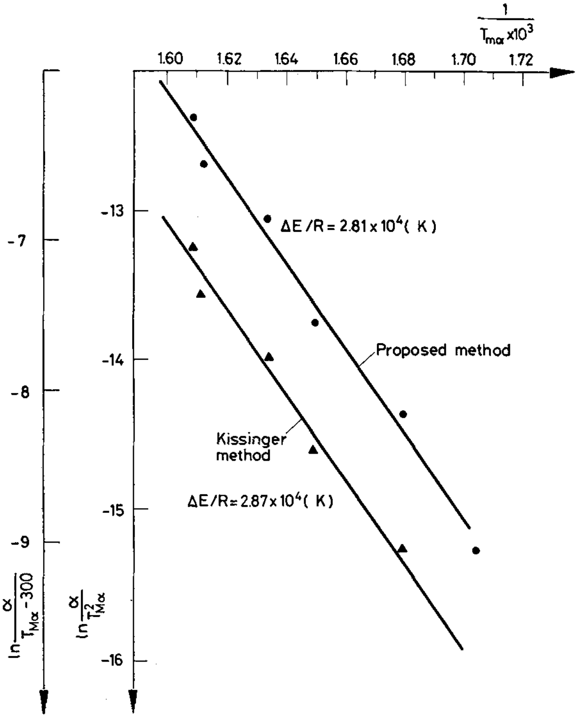

Fig. 2. Determination of $\frac{\Delta E}{R}$ using the modified Kissinger method for tin-nickel. This is a least square fit of Eq. (14). For comparison the erroneous Kissinger plot is also shown

[6]. The electroplated and sputtered deposits are metastable and are known to revert upon heat treatment (7) to the two phases Ni_3Sn_4 and Ni_3Sn_2 which constitute the room temperature equilibrium state of the equiatomic alloy of tin and nickel [8].

Using differential scanning calorimetry the transformation has been found to follow an Avrami law and the parameters n, ΔE, and v were determined [4]. We will compare the results obtained by our modified Kissinger method for DTA with those obtained by DSC.

DTA traces were obtained at six different heating rates on an electroplated sample of tin-nickel. The temperature maxima, $T_{M\alpha}$, and the full width at half maximum, $\Delta\tau_{FWHM}$, of the DTA peaks are shown in Table 1. Figure 2 shows the corresponding modified Kissinger plot

$$\left(\ln \frac{\alpha}{T_{M\alpha}-300} \text{ versus } \frac{1}{T_{M\alpha}}\right),$$

Table 1

Average DTA peak temperature $T_{M\alpha}$, and full width at half maximum $\Delta\tau_{FWHM}$ for different heating rates of "SnNi".

Heating rate, °/min	α, °/sec	$T_{M\alpha}$, K	$\Delta\tau_{FWHM}$, K
2	3.33×10^{-2}	586	16.50
5	8.33×10^{-2}	595	13.50
10	1.66×10^{-1}	606	14.25
20	3.33×10^{-1}	611	14.50
30	5.00×10^{-1}	620	16.50
40	6.66×10^{-1}	621	16.00

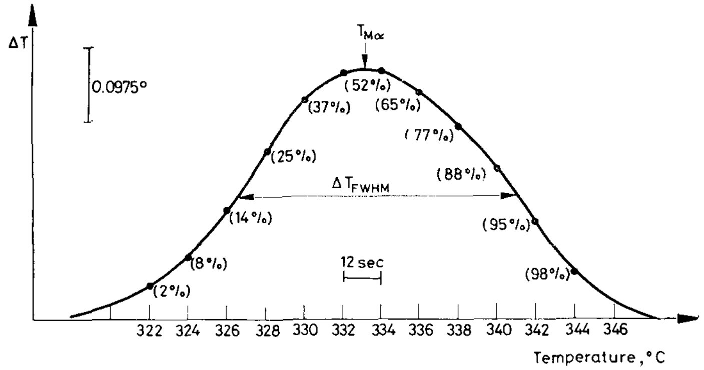

Fig. 3. DTA peak for tin-nickel for a heating rate α = 10°/min. The full width at half maximum used to determine n is shown. Bracketed numbers represent the amount transformed, x, as determined by the Borchardt—Daniels method

from which $\frac{\Delta E}{R}$ and ν are computed by least squares fitting the data to a straight line. The conventional but inapplicable Kissinger plot is also shown for comparison. As stated earlier both plots predict the same value for $\frac{\Delta E}{R}$ but it would be erroneous to apply the conventional Kissinger technique to a situation where Avrami kinetics rule, n is calculated from the values of $\Delta\tau_{\mathrm{FWHM}}$ using Eq. (17). A measurement of $\Delta\tau_{\mathrm{FWHM}}$ for the heating rate of 10°/min is shown in Fig. 3.

Table 2 shows the reaction parameters obtained with our extended Kissinger method. For comparison the results obtained by DSC [4] are also displayed. While the DTA and DSC values for n agree completely, the control values for ΔE and ν are somewhat higher with the DTA method. Reference [4] points out the observed variations of ΔE and ν from sample to sample; the 90% confidence intervals shown in Table 2 intersect for both ΔE and ν and prove our two sets of results to be consistent.

Table 2

Reaction parameters for the transformation of the equiatomic tin-nickel alloy using DSC and the modified Kissinger method for DTA

Avrami parameters	Modified Kissinger method			Differential scanning calorimetry		
	90% confidence interval			90% confidence interval		
	Median	*From*	*To*	Median	*From*	*To*
n	2.2	1.91	2.45	2.1	2.05	2.15
ν, sec^{-1}	2.35×10^{17}	9.8×10^{14}	5.7×10^{19}	6.54×10^{14}	1.3×10^{13}	3.3×10^{16}
F Kcal/mol	56.2	50.7	62.1	47	42	52

The DTA technique has an inherent time lag which depends on the geometry of the measurement cell. This gives rise to the main objection to the Kissinger technique which has been his assumption that the DTA peak occurs at the maximum transformation rate [9]. Using the Borchardt–Daniels technique [10], as is shown in Fig. 3, we found the maximum of the DTA peak to correspond to 55% transformation, while the approximation of our analysis for maximum rate ($kt \approx 1$) would have predicted 63%. The error introduced by using maximum peak temperature instead of the 63% point is believed to be smaller than the normal scatter of the data.

Conclusion

A modification of the Kissinger method suitable for the study of heterogeneous solid state reactions following an Avrami law has been derived and demonstrated. The method gives results comparable to DSC for the determination of the kinetic parameters of the tin-nickel transformation. Although approximate, this DTA method is easier to implement than the Borchardt–Daniels method since it is independent of the parameters of the DTA measurement cell.

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Résumé — Plusieurs expériences isothermes sont en général nécessaires pour déterminer les paramètres de l'équation d'Avrami qui décrit la plupart des réactions hétérogènes en phase solide. Les analyseurs calorimétriques différentiels (DSC) conviennent pour ces expériences. La plupart des appareils d'analyse thermique différentielle (ATD) couvrent un intervalle de température plus grand que les appareils DSC mais ils ne peuvent pas être utilisés pour des études isothermes. Cependant Kissinger a déjà montré comment l'énergie d'activation et le facteur de fréquence pouvaient être calculés à partir d'expériences ATD dans le cas des réactions homogènes suivant une cinétique du premier ordre. La présente publication décrit une extension de la méthode de Kissinger et montre qu'il est possible de l'appliquer aux réactions hétérogènes décrites par une expression d'Avrami. La nouvelle méthode permet d'étudier la cinétique des réactions des phases métalliques dans un domaine de température plus grand qu'avec l'ATD. La cinétique de transformation d'un alliage métastable équiatomique étain-nickel est donnée comme exemple.

Zusammenfassung — Im Allgemeinen werden zur Bestimmung der Parameter der Avrami-Gleichung, welche sich zur Beschreibung der meisten heterogenen Festphasenreaktionen eignet, mehrere isotherme Versuche benötigt. Differential-Scanning-Kalorimeter (DSC) eignen sich für solche Versuche. Während die meisten Geräte der Differential-Thermoanalyse (DTA) ein weiteres Temperaturgebiet umfassen als DSC-Geräte, können sie zu isothermen Bestimmungen nicht eingesetzt werden. Kissinger hatte jedoch bereits gezeigt, wie die Aktivierungsenergie und der Frequenzfaktor aus DTA-Versuchen im Falle homogener Reaktionen erster Ordnung errechnet werden können. In dieser Veröffentlichung wird eine Erweiterung der Methode von Kissinger abgeleitet und ihre Anwendbarkeit auf mit einem Avrami-Ausdruck beschriebene heterogene Reaktionen gezeigt. Die neue Methode ermöglicht das Studium der Kinetik von Metallreaktionen im mittels DTA zu erhaltenden höheren Temperaturbereich. Die Umwandlungskinetik einer metastabilen äquiatomaren Zinn-Nickel-Legierung wird als Beispiel angeführt.

Резюме — В общем, требуется несколько изотермических экспериментов, чтобы определить параметры уравнения Аврами, которое описывает большинство гетерогенных твердотельных реакций. Для таких экспериментов приемлемы дифференциальные сканирующие калориметры (ДСК). В то время как большинство приборов дифференциального термического анализа охватывает более широкую температурную область чем ДСК, они не могут быть использованы для выполнения изотермических определений. Однако Киссинджер показал каким образом активационная энергия и частотный фактор могут быть вычислены из ДТА для случая гомогенных реакций, подчиняющихся первому порядку кинетики. В статье авторы дали развитие метода Киссинджера и показали его применение к гетерогенным реакциям, описываемым уравнением Аврами. Новый метод позволит изучать кинетику металлических реакций в более высокой температурной области чем с ДТА. В качестве примера приведена кинетика превращений метастабильного эквиатомного сплава олово-никель.