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Thermochimica Acta 291 (1997) 59–64

thermochimica
acta

A method for determination of Avrami parameters directly from isothermal calorimetry data

George W. Smith[1]

Physics and Physical Chemistry Department, 2-211 RAB-480-106-224, Research and Development Center, General Motors Corporation, 30500 Mound Road, Bldg. 1-6, Warren MI 48090-9055, USA

Received 24 June 1996; received in revised form 2 October 1996; accepted 8 October 1996

Abstract

A method for determining Avrami parameters directly from isothermal calorimetry data has been developed. Using the method, we have determined values of the time constant τ and exponent n. The τ values agree reasonably well with results from a previous, more cumbersome graphical method of analysis. There are greater discrepancies between the n values derived using the two techniques, presumably due to differences in the magnitudes of time increments by which the data fits are shifted in the two methods. The method is illustrated by analysis of isothermal calorimetry curves for precipitation in several aluminum alloy samples. © 1997 Elsevier Science B.V.

Keywords: Aluminum alloys; Avrami parameters; Calorimetry; Differential isothermal calorimetry; Precipitation

1. Introduction

The kinetics of phase transformations, including diffusion-controlled precipitation, are frequently well described by the empirical equation

$$X(t) = 1 - \exp[-(t/\tau)^n] \tag{1}$$

where $X(t)$ is the fraction of material transformed or precipitated, t the time, τ the time constant, and n a constant [1–4]. Eq. (1) is often called the Avrami equation [4]. Although the exponent n can take on values as high as 4 (or even greater) for various transformations [3,4], it generally lies near 1 for precipitation [1,2,4]. Previously [5], we developed a method for determining the Avrami parameters τ and n from calorimetric experiments for which early-time data are invalid or unavailable, a situation which may arise in certain experimental circumstances (e.g. non-equilibrium conditions following rapid sample warm-up to a heat-treatment temperature). In our studies we determine the kinetics (and energetics) of heat treatment using a Perkin–Elmer DSC2 differential scanning calorimeter operated isothermally [5]. In a typical differential isothermal calorimetry (DIC) experiment, the sample temperature is rapidly increased from ambient to the desired heat-treatment temperature. While the sample is held at temperature, the calorimeter measures dQ/dt, the rate of heat absorption or emission by the sample as a function of time. The resulting dQ/dt plot can be either endothermic (positive) or exothermic (negative), depending on the nature of the thermal process involved. The presence of an endotherm indicates

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[1] Tel.: 810 986 0614; fax: 810 986 3091; e-mail: gsmith@cm-sa.gmr.com.

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PII S0040-6031(96)03096-1

the occurrence of a heat-absorbing event, such as melting or dissolution of a species in a solid matrix. An exotherm is due to some sort of heat-releasing event, such as solidification, precipitation, or an exothermic chemical reaction.

Figs. 1 and are plots of dQ/dt vs. time for precipitation in two samples of an aluminum alloy 339 [6] (data are shown as points; the solid curves are fits which will be discussed later). The plot in Fig. 1 shows dQ/dt at 225°C for a sample which had been air-cooled after casting. As expected, the curve is exothermic, reaching an extremum (minimum) at $\sim$ 2 min and then increasing monotonically toward zero over the next hour or so. In Fig. 2 is plotted dQ/dt at 200°C for a sample which had been water-quenched after casting. In this case the extremum is not reached until 4.8 min after the start of the experiment. From plots like those of Figs. 1 and 2 the total heat absorbed or released by the sample, ΔQ, can be determined by integrating dQ/dt over the duration of the experiment (provided the measurement is continued until the thermal event is complete). During the first minute or so of these calorimetry experiments, data are lost or invalid due to non-equilibrium sample conditions. The method described in ref. [5], developed to correct for this loss of data, is briefly described in the next section, as a basis for discussing an improved Avrami analysis technique which is the subject of this paper.

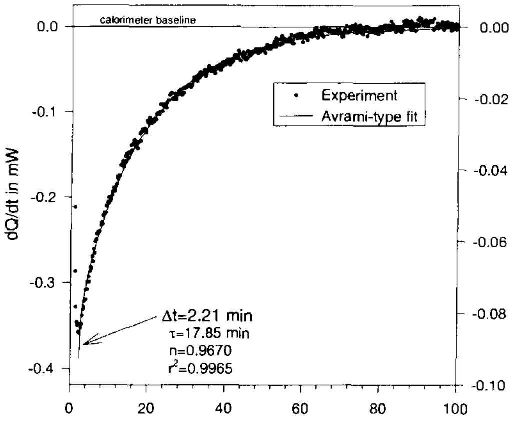

Fig. 1. dQ/dt vs. t at 225°C for precipitation in air-cooled aluminum alloy 339. Curve is best fit of the new Avrami-type analysis directly to calorimetric data for $\Delta t = 2.21$ min.

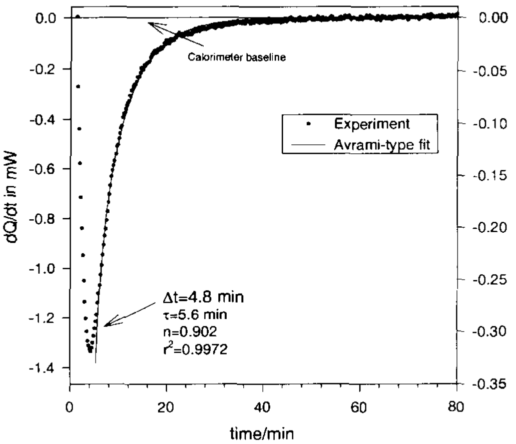

Fig. 2. dQ/dt vs. t at 200°C for precipitation in water-quenched aluminum alloy 339. Curve is best fit of new Avrami-type analysis directly to calorimetric data for $\Delta t = 4.8$ min.

2. Analysis method of ref. [5]

In our previous method [5], determination of $X(t)$ from dQ/dt curves was accomplished by integration of dQ/dt curves after compensating for missing or invalid early-time data. The compensation method involved shifting the dQ/dt data downward in time by an amount Δt (or shifting of the time zero upward by Δt) to place the first valid point at $t = 0$. That is, if data were missing or invalid for an interval Δt_0, we set $\Delta t = \Delta t_0$. $X(t)$ could then be calculated from the time-shifted data using the equation

$$X(t) = \int_0^t (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t \Big/ \int_0^\infty (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t$$

$$= \int_0^t (\mathrm{d}Q/\mathrm{d}t)\mathrm{d}t/\mathrm{const.}. \tag{2}$$

The constants τ and n were evaluated from $X(t)$ using the graphical method [1] in which $\ln(\ln(1/(1-X)))$ is plotted vs. $\ln t$. From Eq. (1) this plot should be a straight line given by

$$\ln(\ln(1/(1-X))) = n\ln t - n\ln\tau \tag{3}$$

The slope of the best fit of Eq. (3) yielded n, and the intercept $n \ln \tau$. In principle, the most reliable results

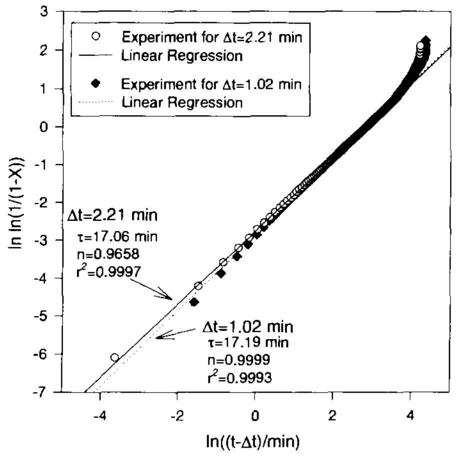

Fig. 3. Graph of $\ln\ln(1/(1-X))$ vs. $\ln(t-\Delta t)$ for sample of Fig. 1. Two plots are shown for $\Delta t = 1.02$ and 2.21 min.

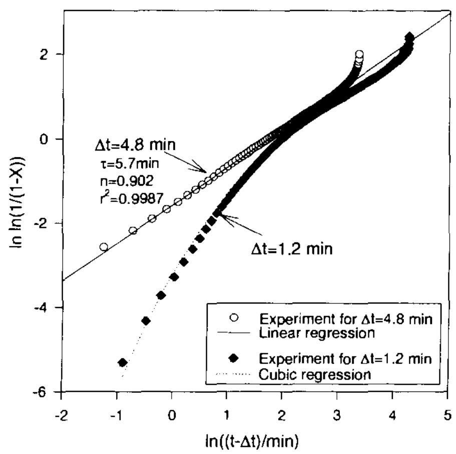

Fig. 4. Graph of $\ln\ln(1/(1-X))$ vs. $\ln(t-\Delta t)$ for sample of Fig. 2. Two plots are shown for $\Delta t = 1.2$ and 4.8 min. Curvature of lower curve shows the importance of proper choice of Δt.

for the Avrami parameters were found from the time-shifted data by determining X-values from Eq. (2) for several different Δt; τ and n values were then calculated for each Δt and plotted vs. Δt. The best values of τ and n were obtained by extrapolating to $\Delta t = 0$ [5]. However, we found that a single determination for which Δt was equal to the time interval over which data were invalid, yielded parameters within roughly ±10% of their extrapolated values. This method is illustrated in Fig. 3, where we plot $\ln(\ln(1/(1-X)))$ vs. $\ln t$ derived from the data of Fig. 1 for two different time-shifts, Δt: 1.02 and 2.21 min. The shorter value of Δt corresponds to the interval of lost/invalid data, the longer is a time increment slightly greater than the position of the extremum of dQ/dt. Although the two plots give comparable values for τ, it appears that the linear regression fit of Eq. (3) is marginally better for $\Delta t = 2.21$ min than for $\Delta t = 1.02$ min (as can be seen from the correlation coefficients, r^2, for the two curves).

The method described in ref. [5] suffers from at least two major drawbacks:

1. Since it involves integration of time-shifted dQ/dt data in Eq. (2) plus a solution of Eq. (3), it is rather time consuming.
2. Furthermore, inasmuch as the fit involves an integral of dQ/dt rather than dQ/dt itself, the user of the method does not obtain an impression of the 'goodness of fit' to the actual calorimetric curves.

This latter point is illustrated in Fig. 4, where we show two plots of $\ln(\ln(1/(1-X)))$ vs. $\ln t$ derived from the dQ/dt curves of Fig. 2 for Δt values of 1.2 and 4.8 min. As in the previous case, the smaller value of Δt corresponds to the time interval for which data are lost/invalid and the larger to the time of the dQ/dt extremum. In this case it is apparent that the larger value of Δt gives much better results: a good straight line fit of Eq. (3) is obtained, yielding Avrami parameters $\tau = 5.7$ min and $n = 0.902$. For $\Delta t = 1.2$ min the curvature of the plot is so great that it is difficult to determine an appropriate time interval over which to perform a fit to Eq. (3); indeed, a cubic fits the data better than a straight line [7].

In the next section we shall describe a method (also involving a time-shift) which compensates for the two drawbacks of the previous method. We shall also present an argument to justify the choice of Δt values comparable to the positions of the dQ/dt extrema.

3. New method: Fit of time-shifted Avrami curve directly to dQ/dt

The basis for the new method is quite straightforward. If we take the derivative of Eq. (2), we obtain

$$\mathrm{d}X/\mathrm{d}t = (\mathrm{d}Q/\mathrm{d}t)/\mathrm{const} \tag{4}$$

Substitution of Eq. (1) into Eq. (4) then yields

$$dQ/dt = -\mathrm{const}\exp(-(t/\tau)^n)(nt^{n-1}/\tau^n) \quad (5)$$

This equation, as it stands, is not in the desired final form for determination of the Avrami parameters. We recall that the best values are obtained from data which is time-shifted. Therefore, we rewrite Eq. (5) to increase the time zero by Δt:

$$dQ/dt = -\mathrm{const}\exp(-((t-\Delta t)/\tau)^n) \times (n(t-\Delta t)^{n-1}/\tau^n) \quad (6)$$

While this equation is formidable in appearance, it can be quickly and accurately fit directly to experimental dQ/dt curves by means of appropriate software, such as TableCurve [8]. One parameter must be determined by inspection of the raw dQ/dt data: the time shift, Δt. In the previous method Δt was taken to be equal to the time interval for which data are missing or invalid. In the present method it is preferable to pick Δt to be comparable to or greater than the time for which the greatest value of the dQ/dt precipitation exotherm occurs. It can be argued that this extremum occurs after an incubation time required for dissolved species to diffuse to a common site where they can react to initiate precipitation. Thus Δt can be taken to be a measure of the incubation time, and the increase of the time zero by Δt corresponds to shifting the origin to the end of the incubation period. Once Δt has been substituted into Eq. (6) in the curve-fitting program, a best fit is obtained which yields the three parameters, n, τ, and const (we are primarily interested in n and τ, and do not report values of const which does not appear in Eq. (1)). In the next section we shall illustrate the method by analyzing several isothermal dQ/dt curves for aluminum alloys.

4. Experimental methods and results of new method

As aforementioned, our experiments are carried out using a Perkin–Elmer DSC2 in its isothermal mode. All samples are run in a nitrogen-filled dry box with nitrogen as the purge gas. In a DIC experiment, the sample temperature is increased rapidly (320°C min^{-1}) from ambient to the desired heat-treatment temperature (generally between 200 and 300°C). After the sample has equilibrated at the selected temperature, the calorimeter records dQ/dt, the rate of heat emission due to precipitation. However, if the calorimeter signal is weak, baseline drift may also contribute to dQ/dt: that is, thermal imbalances between the sample and reference pans of the calorimeter can lead to modest changes (drift) in baseline position over the course of an experiment. We can correct for drift by allowing the experiment to continue longer than the time required for completion of the precipitation process and then extrapolating the long-time baseline back to $t = 0$.

In order to apply the new Avrami analysis method, the digitized dQ/dt data are transferred from the calorimeter to a PC, using file extraction and transfer programs written in our laboratory. The data can then be appropriately manipulated (including correction for baseline drift) and copied to the curve fitting program for determination of n and τ. In the next paragraphs we discuss several examples illustrating the new method.

In Fig. 1 the fit of Eq. (6) to dQ/dt for $\Delta t = 2.21$ min (shown as a solid curve) passes nicely through the data points, yielding Avrami parameters $\tau = 17.85$ min and $n = 0.967$. These values are in reasonable agreement with those derived by the previous method for the same Δt (see Fig. 3). Similarly, the data of Fig. 2 are also well described by Eq. (6) for $\Delta t = 4.8$ min. The resulting Avrami parameters, $\tau = 5.6$ min and $n = 0.902$, agree well with those found using the older method (see Fig. 4). (The small discrepancies in the τ and n values found by the two methods are primarily due to differences in the number of data points used in the fitting process.)

When the signal-to-noise ratio for a calorimetry experiment is low (as may be the case for a slow rate of precipitation or a small amount of precipitate), a good fit may still be obtained. Such a case is seen in Fig. 5. Although the correlation coefficient is small, the best fit of Eq. (6) adequately represents the data.

Eq. (6) does not always provide good fits to dQ/dt. Two examples in which poorer results were obtained are seen in Figs. 6 and 7. In Fig. 6, the fit clearly does not pass through all of the data points. A better fit is obtained by the two-exponential expression discussed

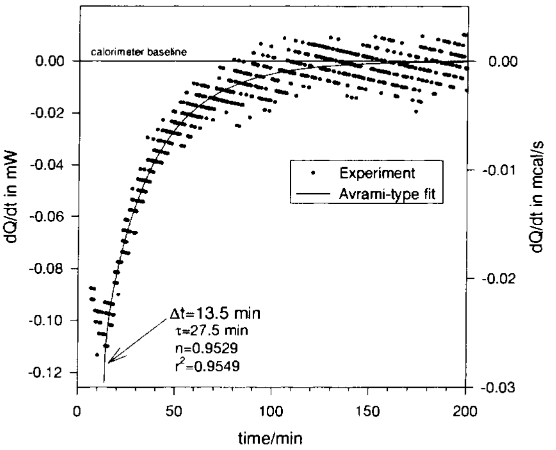

Fig. 5. dQ/dt vs. t at 200°C for precipitation in air-cooled aluminum alloy 339. Although the signal-to-noise ratio is low, fit of new Avrami-type analysis to calorimetric data is good.

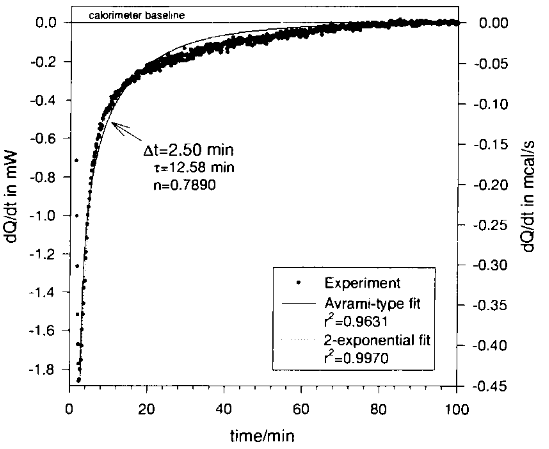

Fig. 6. dQ/dt vs. t at 220°C for precipitation in water-quenched aluminum alloy 339. Best fit of new Avrami analysis is not good. Fit of Eq. (7) is better (two exponentials with $\alpha_1 = 1.188$, $\alpha_2 = 0.1400$, $\tau_1 = 2.07$ min, and $\tau_2 = 22.8$ min).

in ref. [5]:

$$dQ/dt = -\alpha_1 \exp(-t/\tau_1) - \alpha_2 \exp(-t/\tau_2) \tag{7}$$

Here τ_1 and τ_2 are assumed to be time constants for simultaneous precipitation of two different species of solute. A fit of Eq. (7) is shown in Fig. 6 as the dashed curve. In this case the two-exponential fit obviously represents the data better than does the Avrami fit.

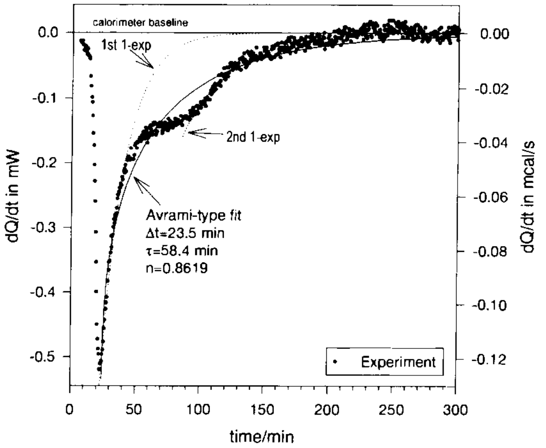

Fig. 7. dQ/dt vs. t at 180°C for solution-treated aluminum alloy 9456 with two sequential precipitation events. Fit of new Avrami-type analysis is poorer than that obtained from two single exponentials with time constants of 18.5 and 38.0 min.

A more dramatic example of a poor Avrami-type fit is seen in Fig. 7. Here we plot an isothermal dQ/dt curve for solution-treated alloy 9456 [9] in which there appear to be two sequential precipitation events. The fit of Eq. (6) does not coincide with the data: the derived τ and n values (58.4 min and 0.8619) are rough averages for both precipitation events. A better representation of dQ/dt is obtained by fitting two single exponentials (dashed curves) to the early- and late-time portions of the data.

A useful comparison of the two methods was obtained by recording dQ/dt curves for precipitation in air-cooled samples of alloy 339 [6] at temperatures ranging from 210 to 300°C. All the resulting isothermal curves exhibited a single precipitation event, like that of Fig. 1, but with time constants which, as expected, decreased with increasing temperature. We evaluated Avrami parameters using both the old and new techniques; The results are compared in Fig. 8 where we plot n vs. τ obtained by the two methods. The Avrami time constants, τ, from the new method are comparable to those obtained using the more cumbersome previous analysis [5]. On the other hand, the n values found by the new method vary much less than those determined by the older method. The older method gives smaller, more scattered n values

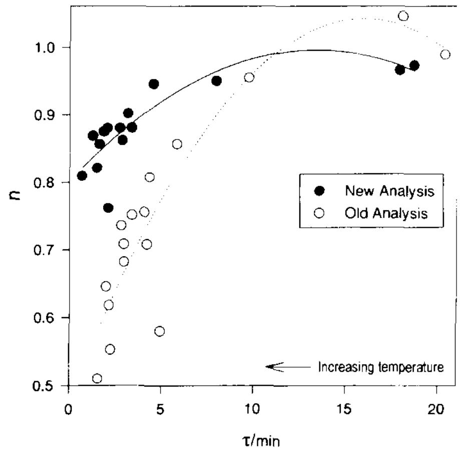

Fig. 8. Plots of n vs. τ derived from new (Eq. (6)) and old (Eq. (3)) Avrami-type analyses. Values of n from the new method lie much closer to 1 and are much less scattered than those from the old method.

for $\tau < 5$ min. We believe that this discrepancy is due to the fact that the older method uses Δt values smaller than the incubation period, leading to greater curvature in plots of $\ln(\ln(1/(1-X)))$ vs. $\ln t$ (as in Fig. 4) [but see also ref. [7]]. The newer method gives n values close to 1 over the entire time constant range. This is satisfying since, as pointed out previously [5], the derived value of τ is less sensitive to the choice of Δt when n is nearly equal to 1.

5. Discussion

The new Avrami analysis described here is often adequate for fitting dQ/dt curves when it appears that there is only a single precipitating species. When two species are precipitating, it may be better to use a two-exponential analysis for simultaneous precipitation events and two single exponentials when the species precipitate sequentially. The choice of analysis to be used can be made by comparison of the correlation coefficients and by visual inspection. If a value of $r^2 > 0.99$ is found using the fit of Eq. (6), the improved Avrami method is probably appropriate; otherwise it may be preferable to use one or the other of the exponential fits. Two factors relevant to the choice of methods should be kept in mind: (1) the two-exponential analysis is probably more physically meaningful than the Avrami analysis in describing precipitation by two species; and (2) the two-exponential analysis is capable of giving a better fit because it has one more adjustable parameter (4 vs. 3).

Given the facts that the new Avrami analysis method is considerably faster than the previous one, that it allows direct comparison with calorimetric curves, and that derived values of n generally lie near 1, we conclude that the new method is an improvement over the old one.

Acknowledgements

The author thanks A.K. Sachdev for useful discussions, for initial information about TableCurve, and for providing samples; W.J. Baxter for suggestions; T.H. VanSteenkiste, S.M. Willett, and R.B. Hall for technical assistance; and D.B. Hayden for computer programs.

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[5] G.W. Smith, Scripta Metallurgica et Materialia 31 (1994) 357.
[6] Alloy 339 contains ~ 1% Cu, ~ 1% Mg, and ~12% Si.
[7] It has been pointed out [J. Malek, Thermochimica Acta, 267 (1995) 81] that the double logarithmic plot used to determine Avrami constants is rather insensitive to subtle changes in the fraction of material transformed. Therefore, its linearity cannot be considered to be a general proof of validity of Eq. (1).
[8] Jandel Scientific, 2591 Kerner Blvd., San Rafael, CA 94901, USA.
[9] Alloy 9456 contains 3.5% Cu and ~ 0.05% Sn. The solution treatment consisted of heating at 527°C for 16 h, followed by a water quench.