Journal of Thermal Analysis and Calorimetry, Vol. 62 (2000) 715–719

KINETIC ANALYSIS OF NON-ISOTHERMAL DSC DATA

Computer-aided test of its applicability

J. Holubová[1], *Z. Černošek*[1] *and E. Černošková*[2]

[1]Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Legií 565, CZ-532 10 Pardubice
[2]Joint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84, CZ-532 10 Pardubice, Czech Republic

(Received April 20, 2000; in revised form August 3, 2000)

Abstract

The applicability of the kinetic analysis of data obtained by non-isothermal differential scanning calorimetry (DSC) is discussed. The Johnson–Mehl–Avrami (JMA) model was used for the computer simulation of DSC traces subsequently analysed by common methods of kinetic analysis of non-isothermal data. For the temperature-independent kinetic exponent n of the JMA equation, the kinetic analysis was shown to provide correct results, e.g. a correct kinetic model and apparent activation energy. On the other hand, for the temperature-dependent kinetic exponent, there is a great possibility of erroneous determination of the correct kinetic model and apparent activation energy, especially at higher heating rates. Since the temperature dependence of n cannot be determined on the basis of non-isothermal DSC experiments, conclusions must be drawn with appropriate caution.

Keywords: computer simulation, DSC, non-isothermal crystallization kinetics

Introduction

Various techniques have been applied to determine the kinetics of first-order phase transformations, e.g. the crystallization of amorphous materials. Calorimetric methods, and in particular differential scanning calorimetry (DSC), are widely used for study of the kinetics of such processes. These methods offer advantages, e.g. they are quite sensitive, not demanding with regard to sample preparation, and relatively independent of the sample geometry. DSC measures a volume fraction transformed as a function of time (isothermal DSC) or temperature (non-isothermal) by measuring the heat released or absorbed during a phase change. In recent years, especially non-isothermal DSC measurements have become very attractive for the study of phase transformations. Non-isothermal experiments can be performed more rapidly than isothermal ones, and they can also be used to extend the temperature range of measurements beyond that accessible in isothermal experiments.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The general theory of transformation kinetics was derived for isothermal transformation conditions [1]. Numerous methods have been developed for the treatment of non-isothermal DSC data in order to obtain kinetic parameters that reproduce the experimental data and predict the behaviour of the system under different conditions [2–4].

As concerns the study of phase transformations involving nucleation and growth under isothermal conditions, analysis of the data obtained has mostly been carried out by using the Johnson–Mehl–Avrami (JMA) formalism [5–7]. This method is based on an integral expression for the fraction transformed:

$$\alpha(t)=1-\exp((-kt)^{\mathrm{n}}) \tag{1}$$

where $\alpha(t)$ is the fraction of the transformation completed at time t, and n is a parameter reflecting the nucleation rate and growth morphology. Rate constant k has an Arrhenius temperature dependence:

$$k=k_0\exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \tag{2}$$

where E is the activation energy, and k_{B} is the Boltzmann constant.

The validity of application of this model to non-isothermal transformation kinetics has been examined by Henderson [2]. He has shown that JMA formalism can be used under specific restrictions that limit the applicability of this formalism to 'site saturation' transformation only. In this case, nucleation takes place at the very start of the transformation, and the nucleation rate is then zero. However, it seems that there are still some problems associated with the correct use of this model for the analysis of non-isothermal data: many papers reveal a great dependence of the activation energy value and variation of the JMA exponent n.

In many cases, the JMA model is unsatisfactory and the non-isothermal transformation kinetics must be described by the Šesták–Berggren (SB) model [8]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}} \tag{3}$$

This model is an empirically found accommodation function. The SB model is a very flexible function with regard to DSC data-fitting, but lacks physical meaning (especially the exponents m and n have no clear physical consequence).

The above-mentioned problems in the analysis of non-isothermal data very probably originate from the fact that the models used for the analysis of non-isothermal DSC data were originally derived for isothermal conditions, and simplifications were introduced to allow these models to be used with non-isothermal data. In the case of the JMA model, the assumption of a constant temperature-independent kinetic exponent n is one of the most problematic simplifications. In our previous study of the isothermal crystallization of As_2Se_3 glass [9], we found a temperature dependence of kinetic exponent n; its value decreased from 3.7 to 1.9 with increasing temperature. The value of n reflects the crystal growth morphology (n~3 in the case of three-dimensional growth, and n~2 for predominantly two-dimensional growth) and was confirmed by optical microscopy.

From this point of view, it can be assumed that, if the kinetic exponent *n* varies with temperature during non-isothermal crystallization, the frequently used kinetic analysis of non-isothermal data does not take this fact into account and erroneous conclusions may be drawn concerning the kinetic model and activation energy.

The purpose of this paper is to contribute to the discussion on the applicability of the commonly used thermal analysis method to non-isothermal crystallization kinetics.

Experimental

Using computer simulation, we have tested the influence of the thermal dependence of kinetic exponent *n* on the shapes of non-isothermal DSC curves.

Three series of DSC curves were computer-simulated, solely on the basis of the JMA model, with heating rates of from 1 to 20 K min^{-1}. The rates used for simulation are commonly used for this type of experiment. A constant apparent activation energy (E=130 kJ mol^{-1}) was used for all DSC curves computed. The first set of curves was simulated by using a constant value of the JMA exponent n (n=2). Further simulations were made with $n=f(T)$; we used a linear thermal relation of n and a stepwise relation between temperature and n, similarly to what was found by means of isothermal experiments [9].

Results and discussion

The curves obtained by computer simulation were successively analyzed in the usual way. This means that the activation energy and subsequently the kinetic model were determined by means of commonly used kinetic analysis.

The following findings emerged:

a) When the value of the kinetic exponent used for computer simulation was constant (n=2), the kinetic model obtained by analysis was of JMA type. The apparent activation energy was independent of α (Fig. 1) and its value could be determined reliably (E=130±1 kJ mol^{-1}). When the analysis was based on the JMA model, the correct value of the kinetic exponent n (n=2) was found.

b) When the value of n used for the computer simulation was not constant, the kinetic model obtained by analysis of the simulated curves was not found unambiguously to be of JMA type, but was mostly of SB type (Fig. 2). The apparent energy value depended significantly on α (Fig. 3), and hence it was impossible to determine the apparent activation energy correctly (the value found was E=118.9±0.9 kJ mol^{-1}). However, for low value of heating rate, it is also possible in some cases to interpret the DSC curves by the JMA model with a temperature-dependent kinetic exponent. The reason for this is the relatively narrow width of the DSC peak at low heating rates when a relatively small change in n occurs in this narrow temperature interval of the phase transformation (Fig. 2).

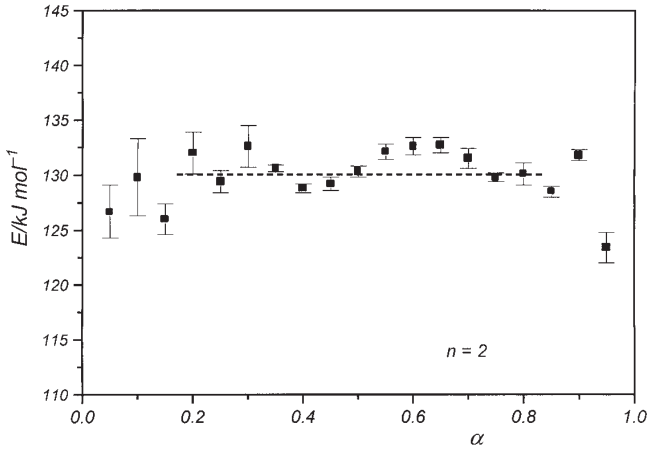

Fig. 1 Values of the activation energy as a function of the degree of conversion α, calculated by the isoconversional method using computer-simulated DSC traces with temperature-independent JMA exponent *n* (n=2). The dashed curve denotes the mean value of the apparent activation energy (E=130±1 kJ mol^{-1})

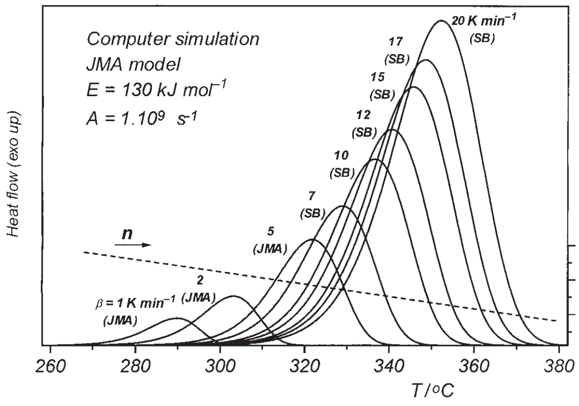

Fig. 2 DSC traces computer simulated with temperature-dependent JMA exponent. The kinetic model found (JMA or SB) is indicated beside each curve

By means of computer simulation of the DSC curves, we have shown that there is still a basic problem involving the extension of originally isothermal transformation kinetic equations to non-isothermal conditions.

It may be concluded that, if the kinetic analysis of non-isothermal DSC curves of crystallization proceeding in fact by the JMA mechanism results in the JMA model, then the model found is most probably a realistic one. In such cases, the value of the activation energy is basically not dependent on α, while its value and that of kinetic parameter *n* reflect the described action.

However, if the kinetic analysis of non-isothermal DSC curves of crystallization results in the SB model, then it is not possible to distinguish whether or not it really

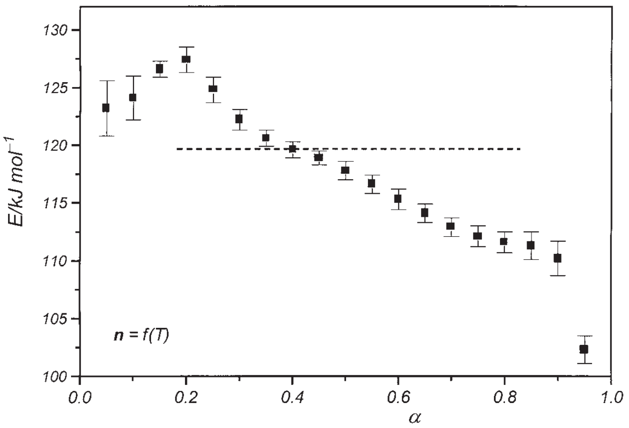

Fig. 3 Values of the activation energy as a function of the degree of conversion α, obtained for DSC traces computer simulated by using a linear temperature dependence of JMA exponent *n* (Fig. 2). The dashed curve denotes the obtained mean value of the apparent activation energy (E=118.9±0.9 kJ mol^{-1})

involves the kinetics of a process that can be described by the SB model or the JMA mechanism with a non-constant value of the kinetic parameter *n*. Our analysis of the simulated DSC curves indicates that a seemingly satisfactory use of the SB model to describe crystallization kinetics proceeding by the JMA mechanism is accompanied by a non-negligible dependence of the apparent activation energy *E* on α.

* * *

This work was supported by project No. 203/99/0046 of the Grant Agency of the Czech Republic.

References

1 J. W. Christian, The Theory of Transformation in Metals and Alloys, 2nd Ed., Pergamon Press, 1975.
2 D. W. Henderson, J. Thermal Anal., 15 (1979) 325.
3 H. Yinnon and D. R. Uhlmann, J. Non-Cryst. Solids, 54 (1983) 253.
4 J. Málek, Thermochim. Acta, 200 (1992) 257.
5 W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Min. (Metal) Engs., 135 (1939) 416.
6 M. Avrami, J. Phys. Chem., 7 (1939) 1103.
7 M. Avrami, J. Phys. Chem., 8 (1941) 177.
8 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
9 E. Černošková, J. Holubová and Z. Černošek, J. Therm. Anal. Cal., 56 (1999) 423.