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The applicability of Johnson–Mehl–Avrami model in the thermal analysis of the crystallization kinetics of glasses[1]

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Abstract

The Johnson-Mehl-Avrami equation is frequently used for analysis of experimental data of non-isothermal crystallization kinetics although this theoretical model has limited applicability for the non-isothermal transformations involving nucleation and growth. It is shown that the applicability of this model should be tested by reliable methods before a quantitative analysis of non-isothermal crystallization data is made. Such testing methods are described and their uses are demonstrated.

Keywords: TA; Crystallization kinetics; Glass; Johnson–Mehl–Avrami model

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1. Introduction

The rather elaborate nature of classical isothermal experimental procedures used to study crystallization kinetics in glasses is probably one of the major reasons for the increasing popularity of thermoanalytical techniques (TA), such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC). Generally, the experimental TA data are analyzed within the framework of the formal theory of nucleation and growth, and then the Johnson–Mehl–Avrami (JMA) equation is applied. However, the JMA equation was developed to describe isothermal conditions and it can be applied to the description of non-isothermal TA data only in a limited number of special cases.

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Therefore, the development of simple, quick and reliable tests of the applicability of the JMA equation are of great practical importance. This is primary purpose of the present work.

2. The JMA transformation equation

The theoretical basis for the description isothermal crystallization of glasses involving both nucleation and growth was formulated by Volmer and Weber [1], Johnson and Mehl [2], and Avrami [3–5]. A similar formalism was also developed by Kolmogorov [6]. A very good review has been given by Christian [7]. In its basic form, the theory describes the time dependence of the fractional extent of crystallization, α. The resulting equation is known as the Johnson–Mehl–Avrami (JMA) equation, and is usually written in the following form:

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

where k and n are constants with respect to time, t. Eq. (1) can be used to describe the transformation kinetics of many solid state processes under isothermal conditions. For some simple cases of crystallization it is possible to find a characteristic value of the kinetic exponent, n, as shown in Table 1 [7].

Table 1

The values of kinetic exponent typical for various crystallization processes in isothermal conditions, after Christian [7]

Transformation	n
(I) Polymorphic changes, discontinuous precipitation, eutectoid reactions, interface controlled growth etc.	
Increasing nucleation rate	>4
Constant nucleation rate	4
Decreasing nucleation rate	3–4
Zero nucleation rate (site saturation)	3
Grain edge nucleation after saturation	2
Grain boundary nucleation after saturation	1
(II) Diffusion controlled growth	
All shapes growing from small dimensions	
Increasing nucleation rate	>2.5
Constant nucleation rate	2.5
Decreasing nucleation rate	1.5–2.5
Zero nucleation rate	1.5
Growth of particles of appreciable initial volume	
Needles and plates of finite long dimensions	1
Thickening of long cylinders (needles)	1
Thickening of very large plates	0.5

Eq. (1) can also be written in a somewhat different form:

$$\alpha = 1 - \exp[-(Kt)^n] \tag{2}$$

The kinetic exponent has the same value in both equations and the constants k and K can be easily converted into each other. The expression in the form of Eq. (2) is used more often because it simplifies subsequent calculations. The isothermal crystallization rate equation (sometimes referred to as the JMA rate equation) can be determined from Eq. (2) by differentiation with respect to time:

$$\mathrm{d}\alpha/\mathrm{d}t = K \cdot n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{3}$$

It should be emphasized, however, that the JMA equation as expressed by Eqs. (1), (2) or (3) is based on several very important assumptions:

(1) isothermal crystallization conditions;
(2) homogeneous nucleation or heterogeneous nucleation at randomly dispersed second phase particles;
(3) growth rate of new phase is controlled by temperature and is independent of time.

These three assumptions should be carefully considered before the JMA equation is used for the description of experimental data and any conclusions concerning the growth morphology are made. Even in the case that all above assumptions are fulfilled, some complementary information (other than just the value of n) are needed for determination of the real mechanism of the crystallization process. Recent computer simulations of crystallization kinetics of randomly oriented ellipsoidal crystals revealed, for example, that for higher crystal anisotropy the dimensionality of growing crystals cannot be unambiguously determined from the value of the kinetic exponent [8].

3. Application of the JMA equation in non-isothermal conditions

It has been shown by Henderson [9,10] and also by DeBruijn et al. [11] that the validity of Eqs. (2) and (3) can be extended to non-isothermal applications if the crystals of a new phase grow from a constant number of nuclei and all nucleation is completed prior to crystal growth. Usually it is expected that the rate constant K in Eqs. (2) or (3) has a simple Arrhenius behavior with respect to temperature during the crystallization process:

$$K = A \exp(-E/RT) \tag{4}$$

where A is the pre-exponential term, E is the activation energy, R is the gas constant and T is the absolute temperature. In this case, however, both the nucleation frequency and crystal growth should have the same (i.e. Arrhenian) temperature dependence. However, this does not seem to be highly probable. From the classical nucleation theory, it follows that the nucleation frequency is strongly temperature dependent, and generally, is very far from Arrhenian [12]. On the other hand, there are some reasons for assigning an Arrhenian temperature dependence to the crystal growth rate. Particularly, in the range of large undercoolings of congruently melting systems, crystal growth rate is inversely proportional to the viscosity of the undercooled melt [13]. The temperature dependence of viscosity of many glass forming liquids can be considered Arrhenian, particularly in a narrow temperature range where the macroscopic crystal growth is usually observed.

The complicated temperature dependence of the nucleation frequency can be neglected in the case of so-called site saturation [14], when the entire nucleation process takes place during early stages of the transformation and becomes negligible afterwards. In this case, the crystallization is an isokinetic process [14]. Thus the crystallization rate is defined only by temperature and it does not depend on the previous thermal history. Under these circumstances, the transformation equations, Eqs. (2) and (3), will hold also in non-isothermal conditions. Some problems arise in the case of glass-forming systems exhibiting high entropies of fusion. Jackson et al. [15] has shown that the secondary nucleation can take place during the growth process. In this case, the applicability of Eqs. (2) and (3) in non-isothermal conditions should be critically examined.

Thermal analysis techniques such as DTA or DSC have become extremely popular methods for studying the crystallization of glasses in non-isothermal conditions. It is assumed that the measured quantity, i.e. the temperature difference between the sample and temperature (for DTA) or heat flow (for DSC) are proportional to the crystallization rate $d\alpha/dt$. This assumption requires that the sample temperature is homogeneous and the growth interface is negligibly affected by the liberation of the heat of crystallization [10]. In the case of DTA, the heating rate, β, changes during the crystallization process. This should be taken into account, especially for larger sample masses and higher heating rates where thermal inertia effects play an important role. For the low crystal growth rates and small latent heat of fusion it is reasonable to assume that both the crystallization rate, $d\alpha/dt$, and the fractional extent of crystallization, α, can be obtained directly from thermoanalytical (TA) data [18].

Experimental TA data are usually interpreted within the JMA model. It should be clearly said, however, that this can be done only in a few cases when the aforementioned conditions are fulfilled. The rate equation used for the description is obtained by combining Eqs. (3) and (4):

$$d\alpha/dt = A\,\exp(-x)f(\alpha) \tag{5}$$

where $x = E/RT$ and $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$. These substitutions are introduced to simplify the subsequent formula.

One of the typical mathematical properties of Eq. (5) is that the Arrhenius parameters are strongly correlated, which means that virtually any TA curve can be interpreted within the scope of several kinetic models by simply varying the activation energy or pre-exponential term [20]. Therefore it is very problematic to use non-linear or multiple linear regression methods for the analysis of TA data assuming a priori the validity of the JMA model. From this point of view, it seems to be important to find reliable testing methods in order to check the applicability of the JMA model in the analysis of non-isothermal TA data.

4. How to test the applicability of the JMA model

Probably the most popular testing method is an inspection of the linearity of the double logarithmic plot of $\ln[-\ln(1-\alpha)]$ as a function of reciprocal temperature $1/T$, which was introduced by Šatava [17] for analysis of non-isothermal TA data. This method involves some substantial simplifications inherent to the non-isothermal formalism and, therefore, it should not be confused with an Avrami plot, i.e. the dependence of $\ln[-\ln(1-\alpha)]$ as a function of time. It is useful to briefly review the derivation of this testing method.

Integration of Eq. (5) in non-isothermal conditions yields

$$[-\ln(1-\alpha)]^{1/n} = \frac{T}{\beta}\pi(x)\cdot A\cdot\exp(-x) \tag{6}$$

where β is the heating rate and $\pi(x)$ is an approximation of the temperature integral [18], which has to be introduced because the exponential term in Eq. (5) cannot be integrated analytically. The rational expression of Senum and Yang [19] is a good compromise between relative simplicity on the one hand and the accuracy of approximation on the other:

$$\pi(x) = \frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \tag{7}$$

Taking the logarithm of Eq. (5) the following equation is obtained:

$$\ln[-\ln(1-\alpha)] = \ln\left[\frac{AT}{\beta}\pi(x)\right]^n - \frac{nE}{RT} \tag{8}$$

Thus, assuming that the term $\ln[AT\pi(x)/\beta]^n$ is a constant, a plot of $\ln[-\ln(1-\alpha)]$ as a function of reciprocal temperature $1/T$ should be linear, having a slope $-nE/R$. It must be emphasized that at least two problems exist if this method is used as a test of the applicability of the JMA model. The first problem arises if for some reason the temperature dependence of the term $\ln[AT\pi(x)/\beta]^n$ cannot be neglected. Then, the corresponding plot will not be linear even in the case that the JMA model is valid. The second problem is associated with the double logarithmic scale itself. It is well known that a double logarithmic function, in general, is not very sensitive to subtle changes to its argument. Therefore, one can expect that the plot $\ln[-\ln(1-\alpha)]$ versus $1/T$ could be linear even in the case of kinetic models other than the JMA. To demonstrate the possibility of a such a wrong interpretation of experimental data, a theoretical TA curve was calculated using Eq. (5) for the Jander's D3 model [18]: $f(\alpha) = 3[(1-\alpha)^{2/3}]/\{2[1-(1-\alpha)^{1/3}]\}$. This TA curve was subsequently analyzed in terms of the double logarithmic plot as shown in Fig. 1. It is seen that data are almost linearly correlated (correlation coefficient is 0.999), and therefore, it could lead to the erroneous conclusion that the JMA model can be used in this case. Thus, the general applicability of the double logarithmic plot for analysis of non-isothermal data should be carefully examined.

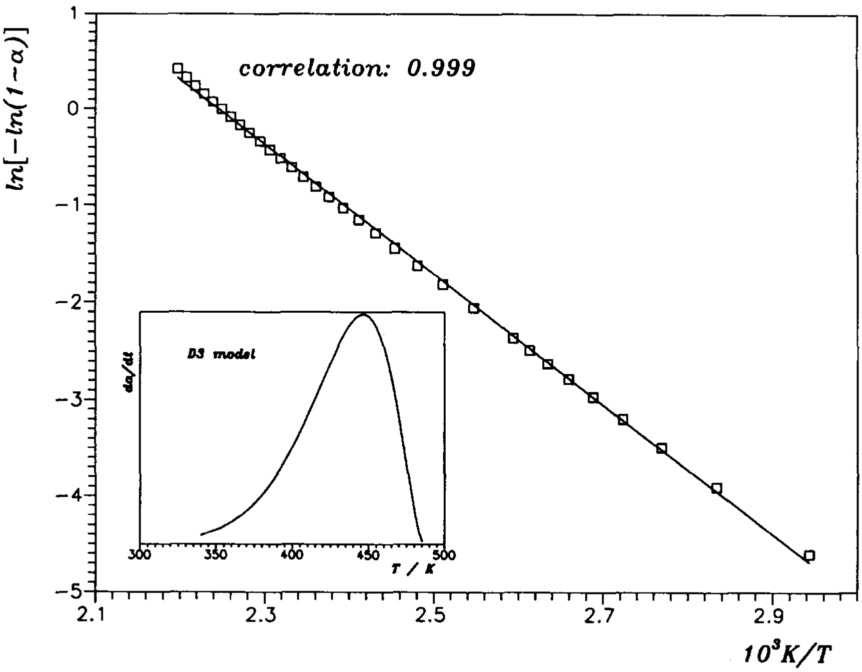

Fig. 1. Double logarithmic analysis of TA curve calculated for the Jander's D3 model ($E = 100$ kJ mol^{-1}, $\ln A = 20$ 1 s^{-1}, $\beta = 10$ K min^{-1}) as shown in the inset.

Another test of the applicability of the JMA model was proposed by Henderson [10]. He has shown that the fractional extent of crystallization at the maximum of the TA peak, α_p, should be close to 0.63 in the case of the JMA model and that it depends only weakly on the kinetic exponent n and the heating rate β. This conclusion was recently analyzed and revised [20], and it was found that the general formula for the maximum of the TA peak can be written as

$$-f'(\alpha_p)\cdot g(\alpha_p) = x_p\pi(x_p) \tag{9}$$

where $f'(\alpha_p) = \mathrm{d}f(\alpha)/\mathrm{d}\alpha$ and $g(\alpha) = \int \mathrm{d}\alpha/f(\alpha)$. These two functions can easily be found for the JMA model. After substitution into Eq. (8), the explicit expression for the fractional extent of crystallization at the maximum of TA peak α_p is obtained:

$$\alpha_p = 1 - \exp\left(\frac{1 - x_p\pi(x_p)}{n} - 1\right) \tag{10}$$

Thus, the parameter α_p does not depend on the heating rate but it depends on both x_p and n. This dependence becomes more important with decreasing x_p, particularly for low values of kinetic exponent n as shown in Fig. 2. Therefore, this test should be applied care-

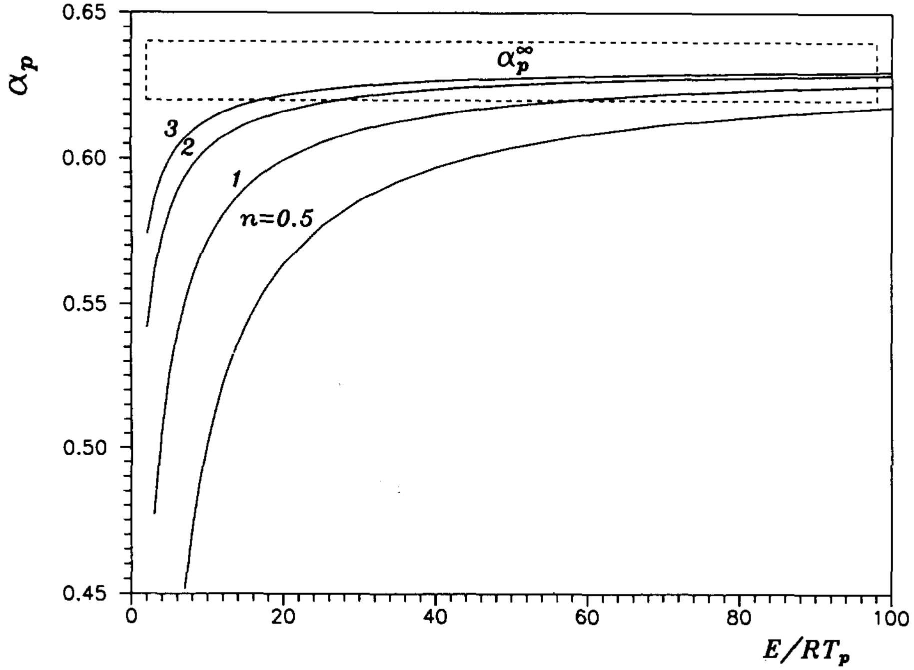

Fig. 2. The dependencies of fraction crystallized at the maximum of the TA peak as a function of E/RT_p for different values of kinetic exponent of the JMA model. The dashed lines show the limits of the maximum of the $z(\alpha)$ function.

fully and one should bear in mind as stated by Henderson [10], "a more rigorous check of the validity would of course be the direct calculation of the JMA transformation rate equation using experimentally determined kinetic parameters and a subsequent direct comparison with experimental trace".

We also believe that the best method is to directly compare theoretically calculated and experimental curves. Unfortunately, this is comparison is still very rare in the literature regardless of the immense development of computational facilities in recent years. From this point of view, simple and reliable testing methods for the applicability of the JMA model have practical importance. Some suggestions in this respect are given below.

5. The maximum of the z(α) function

By substituting Eq. (5) into Eq. (6) the function $z(\alpha)$ can be defined as follows[20]:

$$z(\alpha) = f(\alpha)g(\alpha) = (\mathrm{d}\alpha/\mathrm{d}t)T^2[\pi(x)/\beta T] \qquad (11)$$

It can easily be shown that the $z(\alpha)$ function has a maximum at α_p^∞ defined by the equation:

$$-f'(\alpha_p^\infty)g(\alpha_p^\infty) = 1 \tag{12}$$

(This equation is identical with Eq. (9) for infinite x_p because in this case

$$\lim_{x_p \to 0} x_p \pi(x_p) = 1$$

This is also the reason why the maximum of the $z(\alpha)$ function is usually labeled α_p^∞. In fact, the maximum of the $z(\alpha)$ function corresponds to that of TA peak for infinite x_p.) The solution of Eq. (12) for the JMA model gives the value $\alpha_p^\infty = 0.632$ which is constant for any value of the kinetic exponent n. It was found by numerical simulations that the $[\pi(x)/\beta T]$ term in Eq. (11) has a negligible influence on the shape of the $z(\alpha)$ function. Therefore, the expression for the $z(\alpha)$ function can be substantially simplified:

$$z(\alpha) = (\mathrm{d}\alpha/\mathrm{d}t)T^2 \tag{13}$$

Using this equation, the $z(\alpha)$ function can be obtained by a very simple and quick transformation of the experimental data just by multiplying the crystallization rate by T^2. This can be done without needing to know any kinetic parameter. In this case, the maximum of the $z(\alpha)$ function should be confined to the interval: $0.62 < \alpha_p^\infty < 0.64$ as shown in Fig. 2 by broken lines. Although the range of maximum values of the $z(\alpha)$ function is broader,

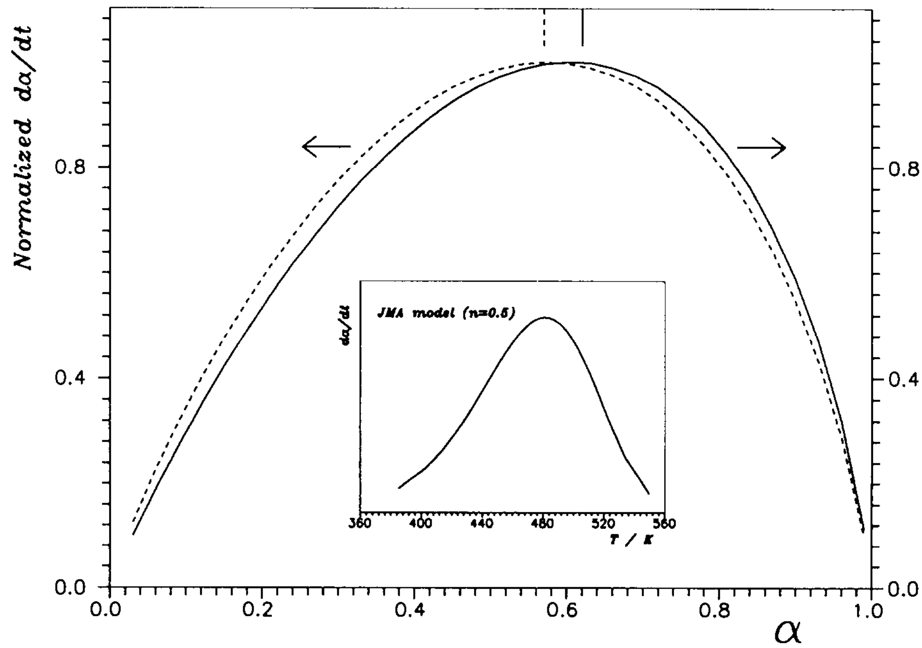

Fig. 3. The normalized TA curve and $z(\alpha)$ function for the TA curve calculated for the JMA model ($n = 0.5$, $E = 100$ kJ mol^{-1}, ln $A = 20$ l s^{-1}, $5 = 10$ K min^{-1}) as shown in the inset.

when compared with the theoretical value of 0.632 corresponding to a more exact expression defined by Eq. (11), it is still possible to unambiguously determine the JMA model by a simple transformation of experimental TA data applying Eq. (13).

To illustrate the practical application of this simple test, a theoretical TA curve corresponding to the JMA model was calculated. Fig. 3 shows both $d\alpha/dt$ and the $z(\alpha)$ values normalized within the interval (0,1) and plotted as a function of the fractional extent of crystallization, α. As expected, the maximum of the $z(\alpha)$ function (full line) is at $\alpha_p^\infty = 0.625$, corresponding well to the JMA model. (The difference from theoretical value 0.632 is caused by an approximation of the $\pi(x)$ function (Eq. 7) used to calculate the theoretical TA curve for the JMA model; see inset of Fig. 3.) On the other hand, the maximum of the normalized $d\alpha/dt$ curve (broken line) is $\alpha_p = 0.575$. According to Henderson's testing method [10], this value could be erroneously interpreted to mean that the data does not correspond to the JMA model. The $z(\alpha)$ function eliminates any ambiguities in this respect. It is convenient, however, to compare $z(\alpha)$ functions for several measurements taken at different heating rates. If normalized plots have identical shapes with a maximum within the range $0.62 < \alpha_p^\infty < 0.64$ then TA data can be probably described within the JMA model.

6. Shape index analysis

The analysis of the shape of TA curves from the kinetic point of view dates back to 1957, when Kissinger [21] tried to determine the reaction order of some decomposition

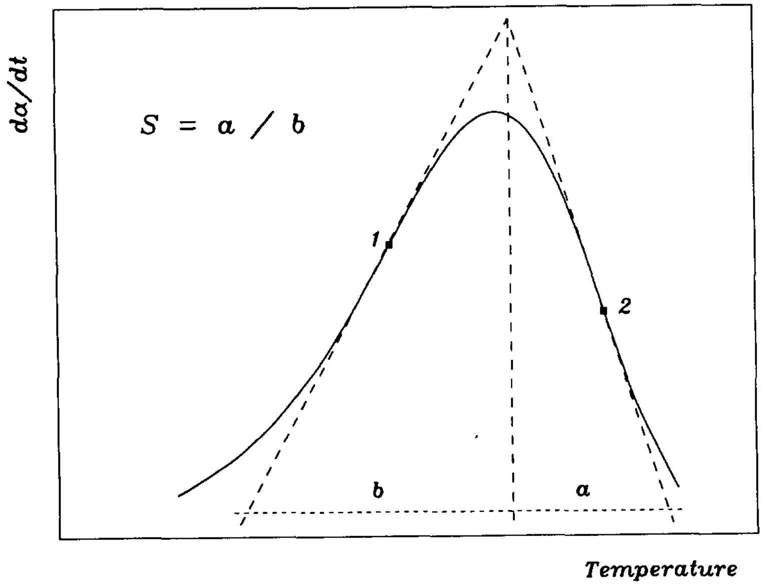

Fig. 4. Method for the determination of the shape index S from a TA curve.

processes by analyzing the shape of the TA curve. The shape index was defined as shown in Fig. 4. Several papers have since been published concerning the shape index analysis of TA curves [22,23]. Recently, it was found by numerical simulations [24] that there is a linear relationship of the shape index versus the inflection temperature ratio (T_2/T_1). This relationship can be described by the equation

$$S = S^{\infty} + K[(T_2/T_1] \qquad (14)$$

where K and S^{∞} are constants for a given kinetic model. The intercept S^{∞} corresponds to the shape index for the infinite value of $x = E/RT$. It can be expressed analytically in the form

$$S^{\infty} = \left| \frac{f(\alpha_1^{\infty})g(\alpha_1^{\infty})[f'(\alpha_1^{\infty})g(\alpha_1^{\infty})+1}{f(\alpha_2^{\infty})g(\alpha_2^{\infty})[f'(\alpha_2^{\infty})g(\alpha_2^{\infty})+1} \right| \qquad (15)$$

where α_1 and α_2 are fractional extents of crystallization at the inflection points of the TA curve. This linear relationship between S and T_2/T_1 is shown in Fig. 5 for the JMA model. In this case the constants in Eq. (14) have the following values: $S^{\infty} = 0.521$ and $K = 0.916$. It should be stressed that for the JMA model the shape index is determined by the T_2/T_1 ratio only and it is not influenced by the value of the kinetic exponent or other

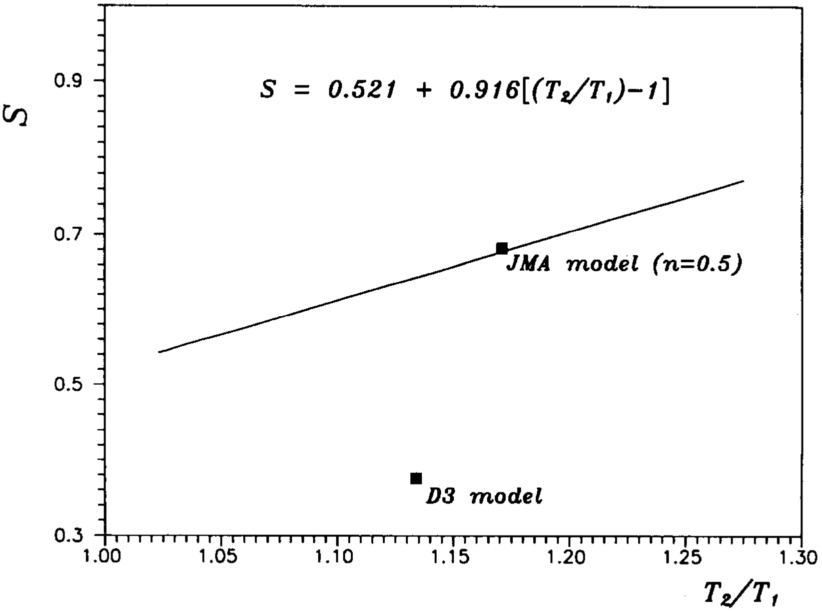

Fig. 5. The dependence of the shape index versus the ratio of temperatures at the inflection points for the JMA model. The points correspond to the TA curves shown in Figs. 1 and 3.

parameters. Because both the shape index and temperature corresponding to the inflection points can easily be determined from an experimental TA curve (or its derivative), this method can also be used for a quick test of the applicability of the JMA model for particular TA data. This is demonstrated in Fig. 5 (points) for TA curves shown in the insets of Fig. 1 and Fig. 3.

7. Empirical kinetic models

In some cases, it is convenient to use more flexible empirical kinetic model functions, $f(\alpha)$, for the description of the crystallization process. The advantage of such an approach is that it is possible to describe experimental TA data even in the case when some of the basic assumptions for the validity of the JMA model are no longer held. These models can also be understood in terms of the accommodation function introduced by Šesták [25], expressing a deviation from the ideal case due to a more complex transformation process. In this respect, it is very convenient to use the Šesták-Berggren function [26,27]

$$f(\alpha) = \alpha^{M}(1-\alpha)^{N} \tag{16}$$

This two parameter function, in fact, also includes the JMA model for $n \geq 1$ as shown in Fig. 6. Thus, if the JMA model can be applied, then the kinetic exponents, M and N,

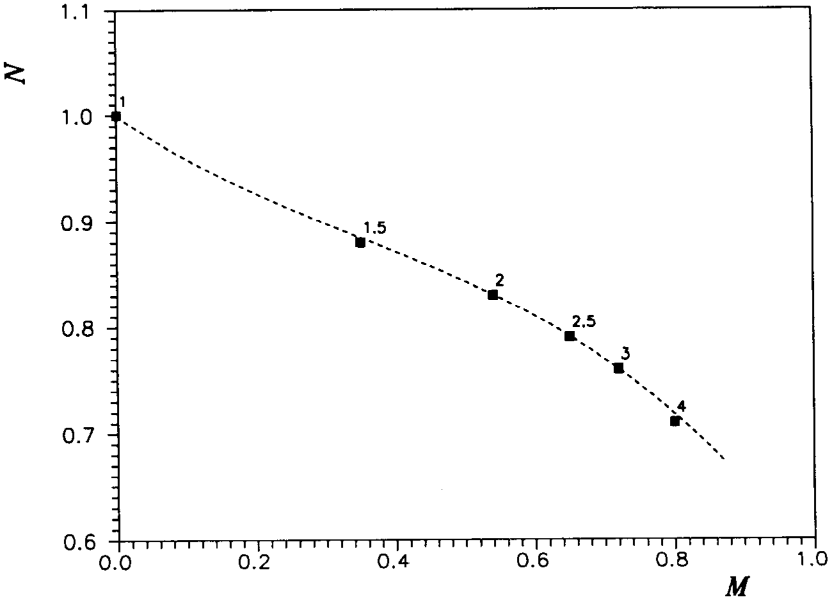

Fig. 6. The combinations of parameters M and N in Eq. (16) corresponding to the values of the kinetic exponent n for the JMA model as shown in Table 1.

should correspond to the broken line in Fig. 6. This can also be considered as an alternative test of the applicability of the JMA model. On the other hand, the departure from the broken line reveals the degree of departure from the JMA model. The Šesták-Berggren empirical kinetic model can be used for a quantitative description of more complicated processes involving both nucleation and growth. Calculated kinetic parameters can be used for the construction of time–temperature–transformation (TTT) diagrams in order to predict the behavior of the system under isothermal conditions. From this point of view, the kinetic exponents M and N in Eq. (16), are characteristic for a particular crystallization process although it is rather problematic to find their physical meaning. It was shown [28], however, that physically meaningful values of the parameter M should be confined in the range $0 < M < 1$.

8. Conclusions

The great number of analyses of non-isothermal TA measurements of crystallization processes which have been published in the literature have suggested the description within the JMA model. Nevertheless, this model is based on several important assumptions and therefore its practical applicability is restricted to particularly simple cases where the site saturation condition is fulfilled. Hence, any quantitative analysis of experimental TA data should be preceded by a rigorous check of the validity of the JMA model. Two simple methods are proposed for such purpose. It is shown that the maximum of the function $z(\alpha) = (\mathrm{d}\alpha/\mathrm{d}t)T^2$ should be confined to the interval $0.62 < \alpha_p^\infty < 0.64$ in the case of the JMA model. An alternative method of testing is based on the linear relationship of the shape index of TA curve versus the inflection temperature ratio (T_2/T_1), which can be written for the JMA model: $S = 0.521 + 0.916(T_2/T_1)$. If these testing methods reveal that the JMA model cannot be applied, e.g. because of considerable overlap of nucleation and growth processes, then the two parametric Šesták-Berggren empirical equation can be used for a quantitative description of the overall crystallization process.

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