1.5.3 KINETIC STUDY OF SOLID-STATE PROCESSES

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Abstract

A simple method for kinetic analysis of solid-state processes has been developed and the criteria capable of classifying different processes are explored. They provide a useful tool for the determination of the most suitable kinetic model. The method has been applied to the analysis of calorimetric data corresponding to the crystallization processes in amorphous ZrO_2. It is found that the crystallization kinetics of amorphous powder sample exhibits a complex behavior under non-isothermal conditions. A two-parameter model provides a satisfactory description of the crystallization process for isothermal and non-isothermal conditions. This enables better control of crystallization extent in fine ZrO_2 powders that is important for preparation of zirconia ceramics with defined properties.

Keywords: kinetics, crystallization, nucleation, growth, calorimetry, zirconium oxide

1. Introduction

The kinetics of solid state processes is generally considered to be a rather controversial topic [1-3]. Most analyses of kinetic data are based on the assumption that the kinetic parameters are intrinsic constants that uniquely characterize a solid-state process under study. This approach may lead to erroneous conclusions as solid-state process usually exhibit rather complex kinetics [4].

There are two main reasons for studying solid-state kinetics despite above-mentioned limitation. One reason is the practical importance of the ability to predict kinetic behavior of a given system under defined conditions. Another reason is related to an understanding of underlying mechanism corresponding to the kinetic process. In the first case we can find a suitable mathematical description for most solid-state processes and, therefore, we may be able to optimize the kinetics. In the second case, however, things are more complicated and the exploration the mechanism of the solid-state process is an uneasy task where a careful study including several complementary experimental techniques and morphological observation is needed.

The rate of chemical reaction is usually expressed to be proportional to the concentration of reactants, raised to a power. In the case of solid-state processes, the concentration is replaced by the fractional conversion α ($0 \leq \alpha \leq 1$). The rate law than can be expressed by a simple differential equation:

$$(d\alpha/dt) = K(T) \cdot f(\alpha) \tag{1}$$

where K(T) is a temperature dependent rate constant and f(α) is an algebraic expression of the kinetic model. There are several simple kinetic models that have been developed on the

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assumption of the simplified geometry of the diffusion processes [5-7], the reaction interface and its spatial movement [8], or the nucleation and growth processes [9-12].

Usually, it is not that difficult to find a suitable rate law from experimental data. However, its interpretation, in terms of underlying kinetic mechanism may be perplexing. For instance, the second-order kinetics of chemical reaction can also result from a complex reaction scheme. The situation is even more complicated in solids where the reactants are spatially constrained, they exhibit irregular shapes, polydispersity, preferred orientations, etc. [4] Under such circumstances, it is reasonable to expect some deviations from the kinetic models mentioned above. This idea led to formulation of empirical kinetic model containing the smallest possible number of kinetic exponents, so that there is yet some flexibility sufficient to describe real data as closely as possible [1,13]. Table I shows two empirical kinetic model (RO,AC) and the Johnson-Mehl-Avrami nucleation-growth model (JMA) that is frequently used for the description of the crystallization kinetics in amorphous solids.

Table I The kinetic models and maxima $(\alpha_y{}^*, \alpha_z{}^*)$ of the $y(\alpha)$ and $z(\alpha)$ functions

Model	Symbol	$f(\alpha)$	$\alpha_y{}^*$	$\alpha_z{}^*$
Reaction order [1]	RO(n)	$(1-\alpha)^n$	0	$1-n^{1/(1-n)}$
Autocatalytic [14,15]	AC(M,N)	$\alpha^M(1-\alpha)^N$	M/(M+N)	$> \alpha_y{}^*$
Nucleation-growth [9-12]	JMA(m)	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$1-\exp(m^{-1}-1)$	0.632

In the following sections we will focus on the analysis of isothermal and non-isothermal calorimetric data corresponding to solid-state processes. A simple method of kinetic analysis will be described. This method than will be applied to the crystallization of amorphous zirconia under non-isothermal conditions and the role of nucleation and growth processes will be discussed. Finally, the conclusion about applicability of the JMA model in non-isothermal conditions will be drawn.

2. The method of kinetic data analysis

The shape and symmetry of the kinetic curve defined by Eq.(1) strongly depends on experimental conditions. The function $f(\alpha)$ should be invariant in this respect. It can easily be separated from K(T) function as shown below using the $y(\alpha)$ function obtained by transformation of Eq.(1). In isothermal conditions this function can be written as:

$$y(\alpha) \propto (d\alpha/dt) = k \cdot f(\alpha) \qquad (2)$$

If the Arrhenius type rate constant is assumed then the $y(\alpha)$ function can be written in non-isothermal conditions as follows:

$$y(\alpha) \propto (d\alpha/dt) \cdot \exp(E_a/RT) = A \cdot f(\alpha) \qquad (3)$$

The E_a is an apparent activation energy that should be determined independently from several experiments conducted at different heating rates [16]. As the parameters k and A in Eqs.(2) and (3) are constants the $y(\alpha)$ function is proportional to the kinetic model. Though the $y(\alpha)$ function is useful, its shape and maximum $\alpha_y{}^*$ (see Table I) does not provide an unambiguous information about the most suitable kinetic model [17].

This is why we need an additional function called $z(\alpha)$ that can be also obtained by a simple transformation of experimental data [17,18]. In isothermal conditions such function can be written as:

$$z(\alpha) \propto (d\alpha/dt) \cdot t = f(\alpha) \cdot g(\alpha) \qquad (4)$$

and the z(α) function can be written in non-isothermal conditions (for Arrhenius rate constant) as follows [18,19]:

$$z(\alpha) \propto (d\alpha/dt) \cdot T^2 = C \cdot f(\alpha) \cdot g(\alpha) \qquad (5)$$

where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$ and the parameter C in Eq.(5) is a constant.
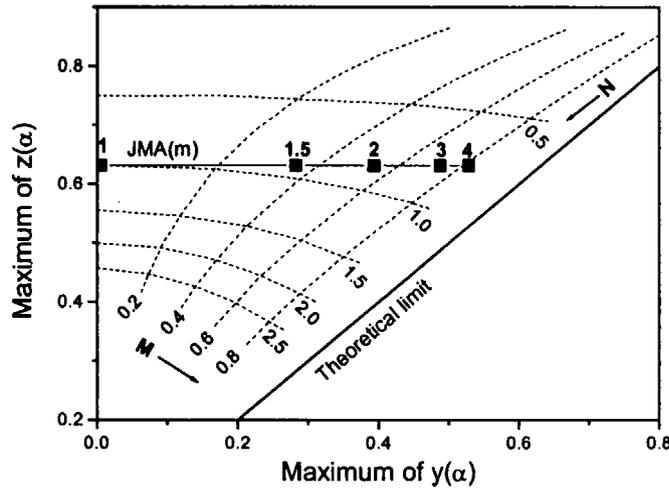
The maxima of the y(α) and z(α) function (see Table I) are characteristic parameters that can easily be used for the kinetic model discrimination. This is shown in Fig.1. It has been shown recently [19] that $\alpha_z^* > \alpha_y^*$ which can be considered as a theoretical limit of any kinetic model (thick solid line in Fig.1).

Fig.1 The kinetic diagram showing the differences between the kinetic models. The broken lines correspond to the different values of kinetic exponents of the AC(M,N) model. The JMA(m) model is represented by points connected by the solid line.

The method of kinetic analysis outlined above has a general validity and it can be used for any type of kinetic data and for most of the f(α) functions. The kinetic diagram is especially effective in the case of a systems that exhibit a complex behavior. Such behavior is observed for example in the case of the crystallization kinetics in amorphous solids [19,20]. In the following section we will show the applicability of this method to the crystallization of amorphous and partially crystalline zirconia.

3. Experimental

An amorphous zirconia was prepared by precipitating a 0.1M stirred aqueous solution of $ZrOCl_2.8H_2O$ with a 1M solution of ammonia added slowly at room temperature. The precipitated hydrated zirconia was washed, filtered and vacuum dried at R.T.

Table II Partially crystallized zirconia samples prepared by annealing at T_{iso} for 1h

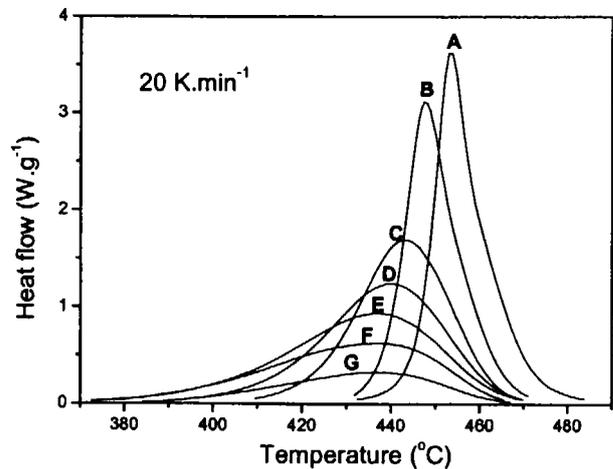| Sample	T_{iso} (°C)	Fraction crystallized
A	-	-
B	340	8 %
C	360	19 %
D	365	22 %
E	367	25 %
F	370	42 %
G	375	66 %

Fig.2 DSC curves of ZrO_2 samples shown in Table II

This partially dried amorphous powder (residual water content 13.7 %) was used to crystallization kinetics measurements by means of Diffrential Scannig Calorimetry (DSC) in a dry nitrogen flow. Partially crystallized samples were prepared by annealing of this powder at different temperatures for 1 hour (see Table II). Crystalline phase identification was performed by using X-ray diffraction (XRD). The morphology of amorphous and partially crystallized samples was examined by SEM and HRTEM.

4. Results and discussion

Fig.2 shows the DSC curves for amorphous sample (A) and partially crystallize samples (B-G) obtained under non-isothermal conditions (heating rate: 20 K.min^{-1}). The maximum of the crystallization peak is shifted to lower temperatures with increasing crystallinity of the sample, probaly due to the fact that the nucleation process is supressed in partially crystalline samples and zirconia crystals grow from preexisting nuclei [21]. Another feature of these data is that the
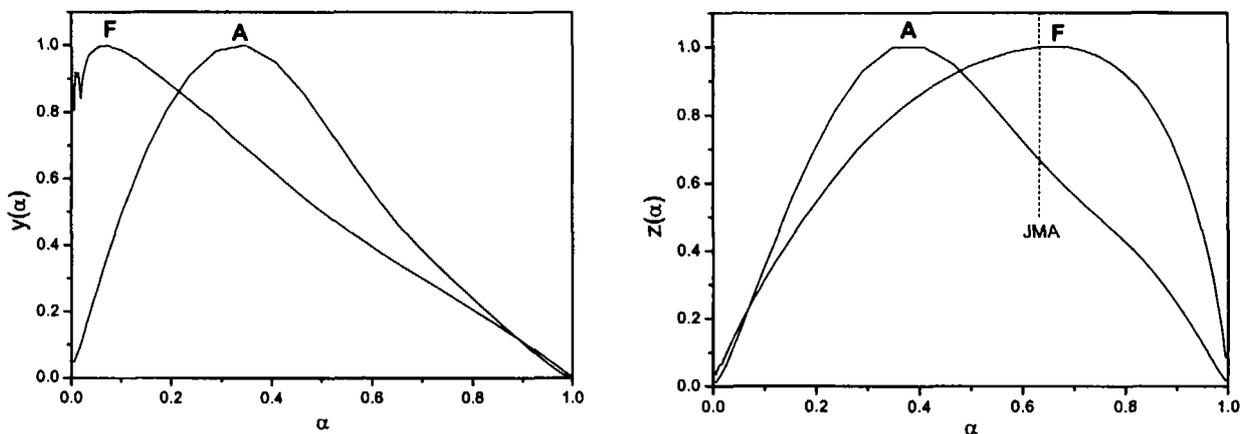

Fig.3 The $y(\alpha)$ and $z(\alpha)$ plots corresponding to amorphous zirconia (A) and partially crystallized (42%) sample (F) calculated by Eqs.(3) and (5) for data shown in Fig.2.

symmetry of the crystallization peak changes as a function of the fraction crystallized. This affects considerably both the $y(\alpha)$ and $z(\alpha)$ function as shown in Fig.3. The apparent activation energy needed to calculate the $y(\alpha)$ function was determined to be 264 ± 11 kJ·mol^{-1} for sample A, and 234 ± 4 kJ·mol^{-1} for sample F [21].

It is evident that the maximum of the $z(\alpha)$ function for sample A is considerably lower than predicted for the JMA(m) model. Nevertheless, there is a shoulder that appears close to 0.632 (see Table I). This rather complicated shape of the $z(\alpha)$ function could be explained assuming that there is non-negligible nucleation during the crystal growth for $\alpha < 0.5$. At higher conversion, however, zirconia crystals are growing from a practically constant number of nuclei. In contrast, the behavior of partially crystallized sample is quite different. The maximum of the $z(\alpha)$ function well corresponds to the prediction for the JMA(m) model. Almost linearly shaped $y(\alpha)$ function suggests that the kinetic exponent should be close to $m = 1$.

A complex crystallization behavior of amorphous (A) and all partially crystallized zirconia samples (B-G) can be visualised in the kinetic diagram shown in Fig.4. The basic part of the diagram is redrawn from Fig.1. The areas confined by by solid lines corresponds to the RO(n) and JMA(m) models. It is assumed that the typical experimental inaccuracy in maxima of the $y(\alpha)$ and $z(\alpha)$ function is ± 0.02.

The total area of the diagram corresponds to the AC(M,N) model.Therefore, the autocatalytic model is a plausible mathematical description of all kinetic models discussed. It is evident that the amorphous sample A exhibits fast self-accelerated crystallization and, therefore, the corresponding point in the kinetic diagram is located near the theoretical limit.
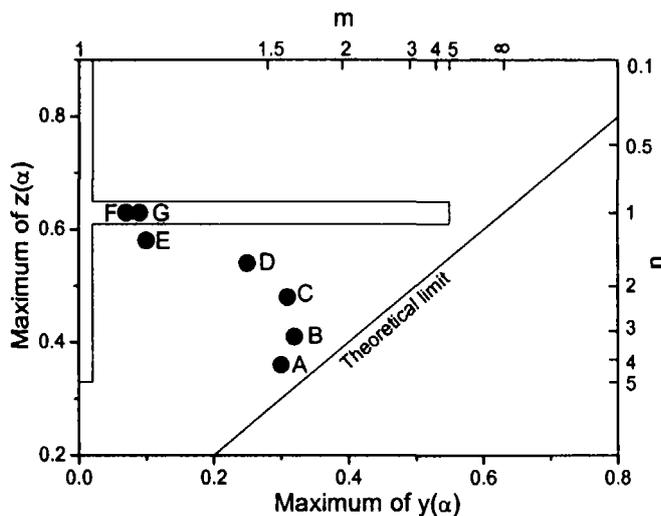

Fig.4 The kinetic diagram for the crystallization of amorphous and partially crystalline zirconia (see Table II). The areas confined by solid lines correspond to the RO(n) and JMA(m) models.

This self-acceleration process gradually slows down in partially crystalline samples (≤ 25 %) as the system approaches the region where the JMA(m) model can be applied (≥ 42 %). The kinetic exponent m is close to 1, which well corresponds to nearly linear dependence of the $y(\alpha)$ function. This value of m is expected in the case of the growth of very small particles dispersed in amorphous matrix. The HRTEM observations revealed that a great number of randomly distributed tetragonal zirconia nanocrystals (approx. 13 nm in size) are formed after heat treatment of as prepared powder [21]. Similar crystal size was estimated from the corrected halfwidth of (011) XRD peak (15 ± 5 nm). The Rietveld analysis of XRD data confirmed [22] that the structure of crystalline phase is very similar to high temperature of t-ZrO_2 [23].

It is obvious that the crystallization process in amorphous amorphous zirconia and partially crystalline samples (< 42%) reveals a complex behavior that cannot be interpreted in terms of the JMA(m) kinetic model. This is easy to understand, because the JMA(m) model is, strictly speaking, only valid under isothermal conditions. Its validity can be extended to non-isothermal conditions [24,25] when the nucleation process takes places during the early stages of transformation, and it becomes negligible during the grystal growth. This seems to be consistent with the fact that the crystallization process in partially crystallized sample F well corresponds to the JMA(m) model. In this case one can expect that the nucleation process is over and the crystals are growing from a practically constant number of nuclei as has been anticipated above. The difference of 37 kJ·mol^{-1} between the value of E_a for amorphous and partially crystalline sample is probably associated with the fact that the nucleation process is no longer operative for a partially crystallized sample.

As we have pointed above, the complex crystallization process in amorphous zirconia can be described by the AC(M,N) model. This is shown in Fig. 5a where the non-isothermal DSC data for amorphous sample are compared with theoretical curves calculated by using Eq.(1), kinetic exponents M = 0.58 $\pm$ 0.08, N = 1.35 $\pm$ 0.05 and Arrhenius temperature dependence of the rate constant. It is assumed that measured heat flow can be written as $\phi = \Delta H \cdot (d\alpha/dt)$, where $\Delta H = 157 \pm 3$ J.g^{-1} is the crystallization enthalpy of amorphous sample. This model can also be used to predict the crystallization extent under isothermal conditions. This is shown in Fig.5b where the experimental data and calculated α-T plots are compared. The isothermal data were obtained by annealing of amorphous sample in DSC instrument at various

temperatures for 1 hour. These samples were subsequently quenched to R.T. and measured at 10 $K.min^{-1}$. The conversion during isothermal annealing was estimated from $\alpha = (\Delta H - \Delta H_i)/\Delta H$, where ΔH_i is the crystallization enthalpy measured after annealing. The curve was calculated by using following equation that can be obtained by integration of Eq.(1):

$$\int_0^\alpha \frac{d\alpha}{\alpha^M (1-\alpha)^N} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot t \qquad (6)$$

It is clearly seen that the AC(M,N) model provides a reasonably good prediction for $\alpha \geq 0.2$, but apparently fails for lower conversions. This seems to be consistent with a complex character of crystallization process in amorphous zirconia.
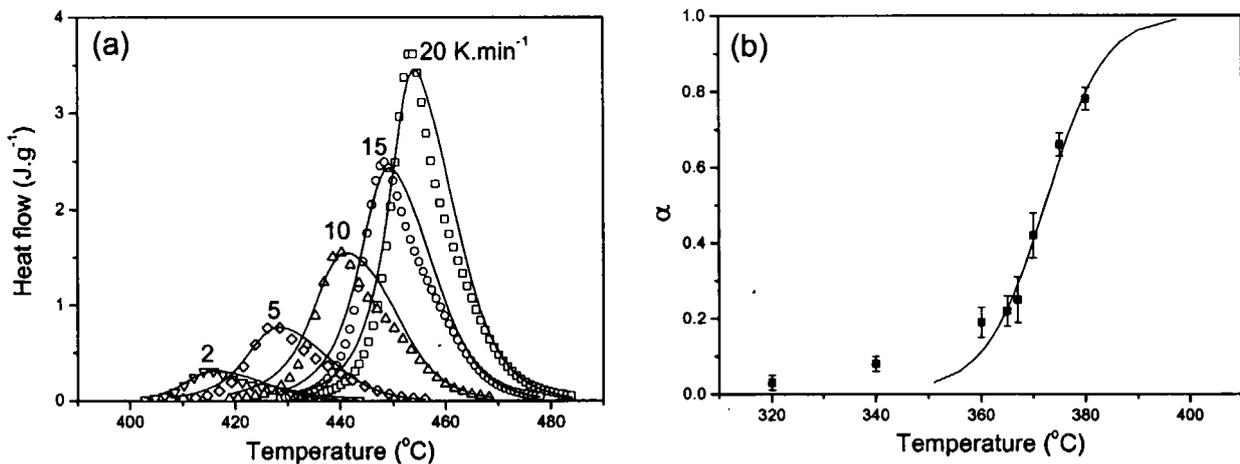

Fig.5 (a) Experimental DSC data for amorphous zirconia sample (points) and curves calculated for AC(M,N) model (solid lines). (b) Crystallization extent for zirconia annealed isothermally for 1 hour at different temperatures (points) compared with the prediction of this model.

5. Conclusions

The results shown above for crystallization of amorphous zirconia clearly indicate that the proposed method based on the kinetic diagram is very useful for the kinetic analysis of solid-state processes. The kinetic diagram helps to visualize the complexity of this kinetic process and provides a useful tool for the determination of the most suitable kinetic model.

It seems that the nucleation and crystal growth processes are overlapped at the beginning of crystallization of amorphous zirconia. As a consequence, the JMA(m) nucleation-growth model cannot be used under non-isothermal conditions, and the two parameter AC(M,N) model should be used instead. This model provides a reasonably good prediction both in non-isothermal and isothermal conditions.

Acknowledgment

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