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EVALUATION OF KINETIC DATA FOR CRYSTALLIZATION OF TiO_2 PREPARED BY HYDROLYSIS METHOD

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Abstract

The formation of TiO_2 prepared by hydrolysis method was presented. Thermodynamics and kinetics of anatase crystallization reaction were investigated. Differential method of kinetic data evaluation in non-isothermal conditions according to Kissinger, Ozawa and Kazeev-Yerofeev was applied. Starting, crystallized and thermally treated powders were determined using X-ray powder diffraction analysis. The characteristic parameters (the activation energy, constant rate and formal kinetic order of reaction) of TiO_2 formation were calculated using DSC data.

Keywords: crystal structure, DSC, oxides, X-ray diffraction

Introduction

It is well known that the study of heterogeneous processes can be investigated by the means of thermal analysis technique. Thermal analysis, as a dynamic method, became a primary source of information concerning reaction kinetics and showed certain advantages compared with the classical isothermal measurements. Differential scanning calorimetry (DSC) is a convenient method for investigating chemical thermodynamics and formal kinetic descriptions of physico-chemical processes. According to DSC theory, the area under the DSC peak is equal to the change of reaction heat [1, 2]. In fact, the principles of thermodynamic and formal kinetic description of processes are based on the generation or absorption of heat during thermal process.

There are many studies on the kinetics of various solid state reactions and phase transformations using DSC analysis [3, 4]. This paper considers the formation of titanium dioxide obtained from titanate precursor by the hydrolysis method.

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Experimental

$TiO_2 \cdot H_2O$ was the starting material for the evaluation of kinetic data. Hydrolysis method was used for the preparation of this compound according to schematic presented in Fig. 1.

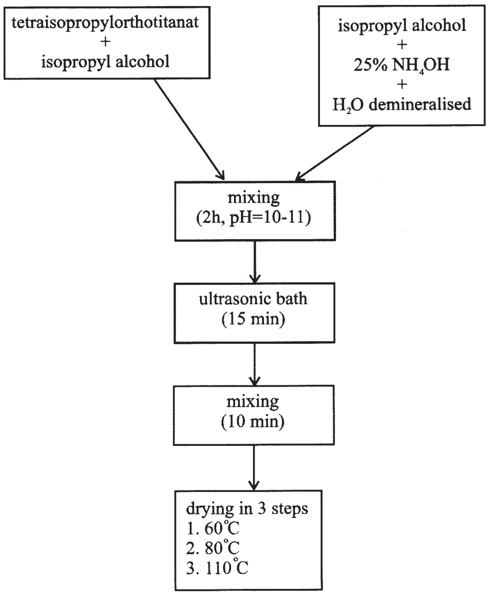

Fig. 1 Hydrolysis method for obtained titanium hydroxide compound

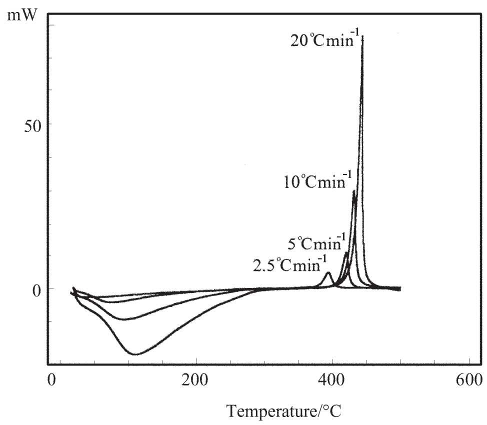

Fig. 2 The characteristic DSC curves for formation of TiO_2

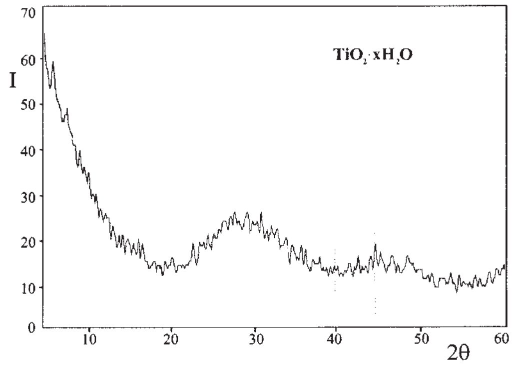

Fig. 3 X-ray diffraction analysis for starting hydrolyzed powders

The crystallization of anatase was carried out with powder samples under nonisothermal conditions up to temperature of 500°C. To evaluate the kinetic parameters for TiO crystallization, the differential scanning calorimetry analysis was performed using Shimadzu DSC-50 analyzer. DSC curves were recorded at the heating rate β=2.5, 5, 10 and 20°C min^{-1} in nitrogen dynamic flow atmosphere. The obtained DSC curves were presented in Fig. 2.

The X-ray powder diffraction patterns (XRPD) were obtained on Philips PW1820 automated diffractometer, using a Cu-tube operated at 40 kV and 35 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter from 5 to 120° (2θ). XRPD experiments were performed at room temperature for starting powders (Fig. 3) and after thermal treatment of powders up to 500 and 900°C (Fig. 4).

Results and discussion

It is well known that the titanium dioxide (TiO_2) exists in three modifications: anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). The former two can be transformed to rutile by heating or even by grinding. Since the rutile presents the most stable crystal structure of TiO_2 many studies on sintering of rutile form of the titanium dioxide were performed. Previously reported literature data for the formation and phase transformation of TiO_2 reveals various informations. For instance, the formation of TiO_2 using DTA method, was examined by several researchers. Houldsworth and Cobb [5] and Kukowski and Kononov [6] have reported two very small exothermic effects at about 730 and 840°C for anatase and rutile, respectively. According to Sullivan and Cole [7], anatase→rutile transformation occurs at about 900°C during heating of colloidal titanium dioxide. Yoganarashimhan and Rao showed that anatase→rutile transformation was carried out at about 750°C with the evaluation of heat exchanged during transformation [8]. The main reason for the disagreement in published data could be the influence of synthesis processes of starting

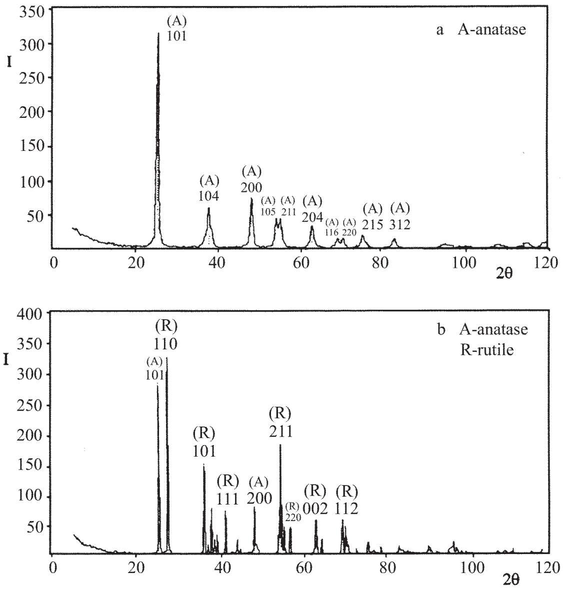

Fig. 4 Diffractogram of TiO_2 powders thermal treated up to 500°C (a) and up to 900°C (b)

powders. Having in mind the influence of synthesis, especially the influence of particle size and their distribution, and poor contact of the reacting particles, it should be assumed that the theoretical model for the evaluation of kinetic parameters could not be applied in general. Hence, the major efforts were mostly spent in testing a large number of equations.

The crystallization process of TiO_2 from amorphous powders could be defined by following relations:

$$TiO_2\cdot H_2O(\text{amorphous}]\rightarrow\text{endothermic processes}\rightarrow$$
$$TiO_2(\text{amorphous})\rightarrow\text{exothermic process}\rightarrow$$
$$TiO_2(\text{crystal})(\text{anatase})\rightarrow\text{exothermic process}\rightarrow TiO_2(\text{rutile})$$

Taking into account these relations and the fact that the formation and phase transformation are very sensitive to processing-related parameters, it is necessary to characterize the starting material using X-ray powder diffraction method. Qualitative X-ray powder diffraction analysis showed only the presence of anatase phase of TiO_2 and pointed to the conclusion that the crystallization process up to 500°C (Fig. 4a) proceeded essentially to the formation of anatase crystal form. Contrary to that, the presence of two phases (anatase and rutile) after heat treatment up to 900°C was observed (Fig. 4b). The quantitative relation between anatase and rutile crystal phases was evaluated by semi-quantitative XRPD method and values of 42 and 58% were obtained, respectively.

On the basis of DSC results (Fig. 2), it could be perceived that the crystallization from amorphous titanium dioxide powders (Fig. 3) to anatase proceeded below 450°C, i. e. at 397, 421, 426 and 433°C for the heating rate β=2.5, 5, 10 and 20°C min^{-1}, respectively. The lattice parameters of the anatase phase (a=3.7852 and c=9.5139 Å) are in agreement with the data obtained by Kumar *et al.* [9] and Yoshinaka *et al.* [10] reported for TiO_2 formed from organic precursor (titanium isopropoxide). Our investigations showed that the anatase obtained from tetraisopropylortotitanate crystallize at much lower temperature (≤450°C in comparison with 600–670°C). These results suggested that as-prepared amorphous powders were consisted of ultrafine particles that enabled lowering of TiO_2 crystallization temperature.

In order to investigate TiO_2 crystallization process the thermodynamic and kinetic analysis by measuring the heat exchange was performed. DSC method, as one of the convenient procedures for the investigation of reaction crystallization, was applied to indicate the enthalpies of TiO_2 formation and crystallization to anatase. Generally, the differences between the obtained values, could be explained by the application of various heating rates. Estimated heat for TiO_2 formation by dehydroxylation reaction was –460±90 J g^{-1} (36.86±6.85 kJ mol^{-1}), while for TiO_2 anatase crystallization heat was 135±15 J g^{-1} (10.73±1.47 kJ mol^{-1}).

Otherwise, in the attempt to investigate the crystallization kinetics, only the crystallization process to anatase can be considered. According to the general scheme for solid state nucleation processes (Fig. 5) and taking into account that the ratedetermined process has to be controlled by diffusion (surface or volume) and/or phase boundary reaction, the formation of TiO_2 could be considered as follows. First, the peak obtained for amorphous TiO_2 powders is characterized by a broad shape leading to the conclusion that the whole process is determined by a rather slow rate. Contrary to that, the crystallization of anatase form of TiO_2 is characterized by a very sharp peak thus pointed to a fast process. It can be assumed that (according to model B) a thin layer of the product propagates fast from the reacting interface into the center of a particle and that the rate-determined process is controlled by diffusion or phase-boundary reaction.

Having in mind that the description of crystallization kinetics presents the problem of finding the dependence of the reaction rate on the parameters that define a given system, it is needful to find, the most common and satisfactory function. In spite of surpassingly extensive literature on non-isothermal methods of kinetic data evaluations, our first attention was given to Kissinger's considerations [11], as a simple differential method able to circumvent difficulties found in many integral methods.

According to Kissinger's method, the fractional conversion of the reactants is constant for a given value of the reaction order – n. The Kissinger equation can be presented as ln dependence:

$$\frac{\mathrm{d}\left[\ln\left(\frac{\beta}{T_{\mathrm{m}}^{2}}\right)\right]}{\mathrm{d}\left(\frac{1}{T_{\mathrm{m}}}\right)}=\frac{-E}{R} \qquad (1)$$

or:

$$\ln\left(\frac{\beta}{T_\mathrm{m}^2}\right)=-\frac{E}{R}T_\mathrm{m}+\ln\left(\frac{RK_\mathrm{o}}{R}\right) \tag{2}$$

where β – heating rate (°C min^{-1}), T_m – peak temperature on DSC curve (K), E – activation energy (kJ mol^{-1}), R – universal gas constant (kJ $°\mathrm{C}^{-1}$ mol^{-1}). K_o is rate constant preexponential factor, established on the well known form of Arrhenius exponential-type function and by macroscopical homogeneous approach description of heterogeneous processes determined as formal kinetic.

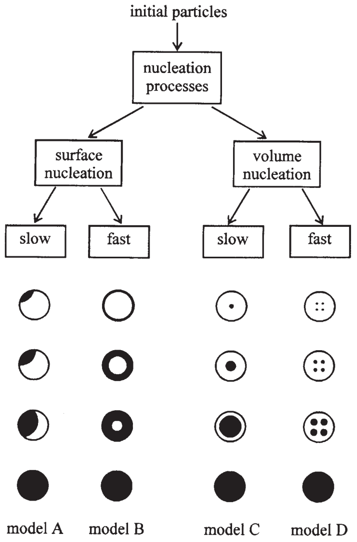

Fig. 5 Solid state nucleation processes

The activation energy corresponding to crystallization, i. e. transition from amorphous state to equilibrium crystalline anatase phase, was determined applying Kissinger's equation. Taking into account data from Fig. 6, presented as a dependence of $-\ln(\beta/T_\mathrm{m}^2)$ *vs*. $1/T_\mathrm{m}$, the activation energy (E) and rate constant (K_o) was calculated 160±2 kJ mol^{-1} and $2.86\cdot10^{11}$ min^{-1}, respectively.

Using Ozawa's equation [12], as a similar mathematic diferential method for determination of the activation energy, in the form:

$$\ln\beta=C-\frac{E}{RT_\mathrm{m}} \tag{3}$$

and the data from Fig. 7, it was evaluated that the activation energy was 171±3 kJ mol^{-1} and $K_\mathrm{o}=5.27\cdot10^{13}$ min^{-1}.

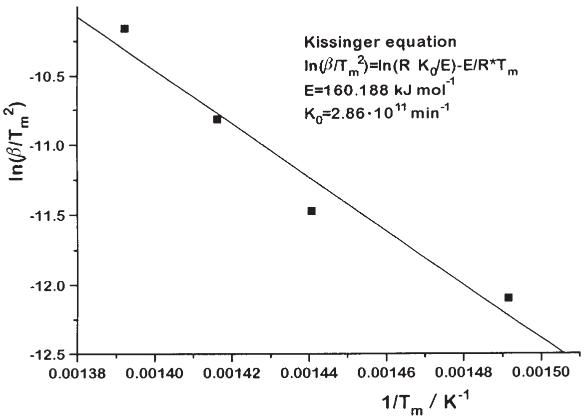

Fig. 6 Employing Kissiger's equation on anatase crystallization process

It should be noticed that those two differential equations gave practically the same values of the activation energy, regardless the fact that Kissinger's equation is completely valid only if the reaction order n is equal to 1. Kissinger developed a shape index s, defined as the absolute value of the ratio of the tangents to the differential curves at the inflection points, and related it to the reaction order by the equation n=1.26 $s^{1/2}$. For the crystallization of TiO_2, from the inflection points of the integral curves n was calculated to be $2<n<3$.

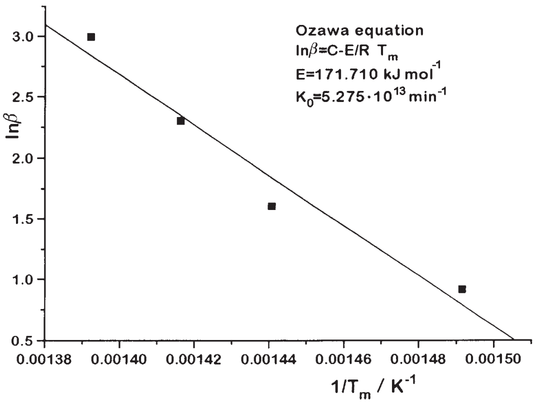

Fig. 7 Employing Ozawa's equation on anatase crystallization process

Non-isothermal kinetic analysis of TiO_2 crystallization has to be employed using mathematical interpretation of the dimensionless degree of reaction in stationary point – α_m. The main theoretical problem in non-isothermal kinetics is to establish the relation between α_m, and the heating rate β during reaction. Taking into account that α_m is the constant parameter of stationary point in non-isothermal kinetics, and also independent of the heating rate, it could be possible to establish a quite simple equation. According to that, one of the convenient procedure could be Kazeev-Yerofeev's equation [13]. From the formal mathematical viewpoint, Kazeev-Yerofeev equation is applicable for the description of non-isothermal kinetic curves for every point of the curve, as well as for the stationary point.

With the change of the heating rate, according to Horowitz-Metzger procedure [14], temperature of stationary point T_m – maximal temperature, also changes, while other kinetic parameters, including α_m, have to be constant. From the differential form of Kazeev-Yerofeev equation [13]:

$$\frac{d\alpha}{dt}=k(1-\alpha)[-\ln(1-\alpha)^{(n-1)/n}] \tag{4}$$

three kinetic parameters could be determined: activation energy – E, rate constant – K_o and the parameter that characterize the order of reaction – n.

Applying Kazeev-Yerofeev equation [13] on experimental results of TiO_2 crystallization for each heating rate, in the form:

$$\ln[-\ln(1-\alpha)]=\frac{nE}{RT_m^2}\theta \tag{5}$$

where $\theta=T_i-T_m$ (T_i – current reaction temperature), and presenting $\ln[-\ln(1-\alpha)]$ as a function of θ, the slope of the straight line is:

$$\mathrm{tg}\varphi=\frac{nE}{RT_m^2} \tag{6}$$

By solving the following three equations:

$$nE=RT_m^2\mathrm{tg}\varphi \tag{7}$$

$$\frac{K_o}{\beta}=\frac{RT_m^2}{nE}\exp\left(-\frac{E}{RT_m}\right)=1 \tag{8}$$

$$\mathrm{tg}\varphi=\frac{K_o}{\beta}\exp\left(-\frac{E}{RT_m}\right) \tag{9}$$

parameters E, K and n it can be determined.

Actually, K_o and E can be defined by relation:

$$\ln(\beta\mathrm{tg}\varphi)=\ln K_o-\frac{E}{RT_m} \tag{10}$$

and parameter – n from the Eq. (6). The results are presented in Fig. 8.

Employing previously mentioned Kazeev-Yerofeev equations, the activation energy which corresponds to anatase crystallization is 181±2 kJ mol^{-1} and $K^o=4.38\cdot10^{13}$ min^{-1}. It can be noticed that the value of n vary ($2.25\leq n\leq3$) which was one of the assumptions for applying this equation.

Taking into account that temperature dependence of n is not significant, Gorbachev [14] proposed that the activation energy could be determined by using equation:

$$E = \frac{RT^2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\beta(1-\alpha)[-ln(1-\alpha)]} - \frac{\bar{n}RT_2}{t\beta} \tag{11}$$

where $\bar{n}$ – an average value of n. According to literature data, this relation is correct only in the case when more than one differential curves exist. It could not be applied to TiO_2 anatase crystallization.

Finally, the application of non-isothermal kinetic analysis of DSC results for kinetic description of anatase crystallization gives a mathematical expression of some hypothetical model chosen to represent the investigated process. The derived kinetic parameters for TiO_2 crystallization are in relatively good agreement with the proposed model. In this single phase system homogeneous nucleation process was indicated, i. e. the ratedetermined process had to be controlled by diffusion and phase boundary reaction ($n\neq1$). Having in mind that value of n is $2<n<3$ it could be supposed that the rate control mechanisms of nucleation processes for anatase crystallization were two- and three-dimensional diffusion.

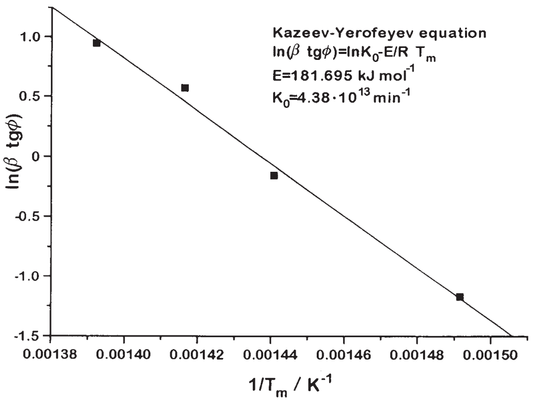

Fig. 8 Employing Kazeev-Yerofeev equation on anatase crystallization process

Conclusions

It was shown that the thermal formation of TiO_2 as-prepared from tetraisopropylortotitanate by hydrolysis method was carried out in two steps: amorphous TiO_2 (up to 350°C) and anatase (420–450°C). Phase transformation of anatase to rutile was not performed to the end up to the temperature of 900°C. It was calculated that the heat of TiO_2 formation (enthalpy) by dehydroxylation reaction and anatase TiO_2 crystallization were -460 ± 90 kJ g^{-1} and 135 ± 15 J g^{-1}, respectively.

Non-isothermal methods of kinetic data evaluations were used for kinetic considerations. Differential methods according to Kissinger, Ozawa and Kazeev-Yerofeev were applied. The activation energy – *E*, constant rate – K_o and formal kinetic order of reaction – $\bar{n}$ were calculated for anatase crystallization process.

According to applied kinetic equations (Kissinger, Ozawa and Kazeev-Yerofeev) *E* was 160, 171 and 181 kJ mol^{-1}, K_o had values $2.86 \cdot 10^{11}$, $5.27 \cdot 10^{13}$ and $4.38 \cdot 10^{13}$ min^{-1} and $\bar{n}$ was 2.5 and 2.81, respectively.

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