

INVESTIGATION OF THE NON-ISOTHERMAL KINETICS OF THE FORMATION OF ZnFe_2O_4 AND ZnCr_2O_4

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Abstract

The kinetics of ZnFe_2O_4 and ZnCr_2O_4 formation under non-isothermal conditions using DTA is discussed. It was determined activation energy and kinetic model for studied reactions in the case of used various sources of starting materials (ferric pigments, chromic oxides). The activation energies for ZnFe_2O_4 are positioned in a range of 200–475 kJ mol^{-1} (in dependence of used ferric pigments) and in case of ZnCr_2O_4 in a range of 130–160 kJ mol^{-1} . The autocatalytic kinetic model (Šesták-Berggren) was found to be the most convenient description of the studied processes.

Keywords: activation energy of ZnFe_2O_4 , pigments, spinels, study of kinetic models, zinc ferrite, ZnCr_2O_4 formation

Introduction

A series of oxidic materials, such as fireproof ceramics, ferrites, ceramic pigments, and the like [1] are prepared by solid-phase reactions by calcination at high temperatures (800–1800°C) [1, 2]. In case of the spinel-like compounds, ZnFe_2O_4 and ZnCr_2O_4 , the calcination temperature varies in a range of 1000–1250°C [2]. Such compounds may be used as ceramic pigments [2]. ZnFe_2O_4 is further used for producing ferrites [1] and it has been produced even as an anticorrosive pigment [3, 4] recently.

A number of authors were engaged in the problem encountered in investigating the formation of such compounds. There can be used the method of thermal analysis [5–9], chemical analysis [10, 11] and X-ray diffraction analysis [11, 12]. The methods used affect also the values of activation energy as determined by individual authors. In case of ZnFe_2O_4 the values fluctuate in a range of 58–461 kJ mol^{-1} [6]. The temperatures of the course of reaction (determined by DTA procedure) vary in a range of 600–800°C [6]. Paulik [7] reports a range of 570–750°C. The activation energies for the formation of

ZnCr₂O₄ vary in a range of 67–272 kJ mol⁻¹ [13]. Both spinel compounds are formed from single oxides ZnO and Fe₂O₃, resp. Cr₂O₃. The differences between individual values of activation energy are connected with the state of crystal lattice of raw materials (reactants) used (structural defects, the way of their formation etc.). Briefly said there may be found differences caused by their various reactivities.

Reactivities of the starting compounds can be enhanced via the activation by grinding on the hand [14–16] and further by the conditions of preparing of the starting materials on the other [16, 17]. The authors [17] prepared Fe₂O₃ balloons by calcination of ethylene glycol solutions of FeCl₃, the reactivity of the compound being much higher than that of Fe₂O₃ prepared by calcination of amorphous iron hydroxide.

This paper deals with various kinds of Fe₂O₃ and Cr₂O₃ and therefore of various reactivities and their influence of the final pigments properties.

Kinetic analysis

In addition to determining the activation energy influenced through the various reactivities of starting oxides it is desirable to find an appropriate model describing the kinetics of the formation of spinel-like compounds. In most cases the Jander and Ginstling-Brounshtein equation [11, 18] is found appropriate; paper [6] reports that the reaction of ZnO and Fe₂O₃ is satisfied most closely by the Avrami nucleation equation.

An original method was elaborated for determining the kinetic model of the reaction based on measuring the DSC or, occasionally, the DTA curves [19–23]. This method is based on the following assumptions. It is assumed that the measured heat flow can be expressed as:

$$\Phi = \Delta H A e^{-E/RT} f(\alpha) \quad (1)$$

where ΔH is the enthalpy change, A is a pre-exponential factor and E is the apparent activation energy. The function $f(\alpha)$ in Eq. (1) represents the kinetic model of the process.

The main problem encountered on seeking the kinetic model consists in mutual kinetic-parameter and $f(\alpha)$ function correlations. Therefore it is to be recommended to measure the process when various heating rates are used. The kinetic analysis consists there in determining the activation energy and kinetic model parameters on independent ways. The calculation of activation energy is possible using the Kissinger, Friedman, Ozawa method [20]. For determining the kinetic model two special functions, $y(\alpha)$ and $z(\alpha)$, were defined. These functions can be obtained by a simple transformation of experimental data. The functions are defined as follows [19–21, 29, 30]:

$$y(\alpha) = \Phi e^{E/RT} \quad (2)$$

$$z(\alpha) = \Phi T^2 \quad (3)$$

These functions are usually normalized within (0.1) interval [20]. Both of these functions can be used to determine the most possible kinetic model that corresponds to the process under study. Once the kinetic model has been determined the kinetic

exponent and the pre-exponential factor can easily be calculated. The methods of calculation are described more in detail in earlier papers [19, 22, 30] (appendix too).

With respect to the fact that there are many kinds of ferric oxides (produced as commercial pigments) and chromic oxides differing in the art of their preparation the main interest of our experiments (and of our paper too) is therefore concerned in methods of evaluation of reactants reactivity (e.g. onset temperature and activation energy when DTA methods are used) and the possibilities of its influencing.

Experimental

Starting materials

Altogether 8 kinds of commercial pigments (5 ferric oxides and 3 chromic oxides) were investigated as raw materials for the spinel formation, pigments bearing the following designations: ferric red TP 303 (Precheza Přerov, Czech Republic), ferric red FB 110 (Bayer AG Company, Germany), ferric red FB 130 (Bayer AG Company, Germany), ferric yellow Hrušov (Hrušov Chemical Company, Czech Republic), ferric yellow B 920 (Bayer AG Company, Germany), Cr₂O₃ Acrox (Glazura Company, Roudnice nad Labem, Czech Republic), Cr₂O₃ Bayer GX (Bayer AG Company, Germany) and Cr₂O₃, p. a. (Lachema Company, Brno, Czech Republic). In parentheses the Producer or Marketing Company is given for each of these pigments. As a ZnO source Zinc White GR of the Heubach Company (Germany) was used. The starting oxides Fe₂O₃, FeO(OH), Fe₃O₄, Cr₂O₃ and ZnO are produced commercially as well known coloured pigments for application in paints and plastics (the purity 98–99 mass% of active oxide).

Preparation of reaction mixtures

A weighed amount of 10 g equimolar mixture of ZnO and Fe₂O₃ (the amount of ferric yellows being related to equivalent amounts of Fe₂O₃) or ZnO and Cr₂O₃ was homogenized under wet conditions in a Fritsch planetary mill Pulverisette 5 for 1 h. There were agate mortars used of a volume of 50 ml and 6 agate balls 1–1.5 cm in diameter. The reaction mixture was dried in a drier at a temperature of 100°C and pulverized in a porcelain mortar.

Differential thermal analysis (DTA)

All the prepared reaction mixtures were subjected to a DTA procedure using a Derivatograph C (Hungary) operated under the following conditions:

Sample masses: 300–600 mg, temperature range 25–950°C, linear heating rates 8, 10, 12 and 15 K min⁻¹ (in case of ZnFe₂O₄) or 8, 10, 12 and 14 K min⁻¹ (in case of ZnCr₂O₄), air atmosphere, reference substance – aluminum oxide for thermal analysis. The samples were placed in an open corundum crucible, the temperature being taken by means of a Pt–PtRh thermocouple. The records of DTA curves were taken in co-ordinates ΔT vs. T . In the interest of determining the kinetics parameters the TAS program [19] was used. Due to the fact that the reaction peaks obtained are very low

the signal values were treated for subsequent signal processing by multiplying using a factor of 10. This mathematical operation is of no influence on the kinetic model parameters.

Specific surface

The specific surface value was measured using a Micromeritics Rapid Surface Area Analyzer Model 2200 A. The samples were de-aerated at 100°C for 60 min. Nitrogen was used as a sorption gas.

Results and discussion

As already stated above, the reaction mixtures of ZnO and Fe₂O₃ (or, occasionally, FeO(OH) and ZnO) and Cr₂O₃ were investigated using a DTA procedure. With all the samples exothermic peaks corresponding to the formation of ZnFe₂O₄ or ZnCr₂O₄ are observed. In case of ferric yellows it is possible to observe in addition to these peaks also distinct endothermic peaks corresponding to the dehydration of the appropriate pigments. In case of the ferric yellow Hrušov this peak can be observed in a temperature range of 250–397°C, and the ferric yellow B 920 shows it in a temperature range of 247–420°C.

All the reaction mixtures were investigated at 4 heating rates (β). The growing of heating rates are accompanied with shifts of the reaction peak maxima. In Fig. 1 there is an example given of the DTA curves obtained with the ferric yellow Hrušov. In Tables 1 and 2 the followings are given, for individual pigments under investigations, the extrapolated temperature values for the reaction start ($T_{\text{ons } 1}$), and the reaction end ($T_{\text{ons } 2}$), the temperature of peak maxima (T_p), and the peak areas (P). Activation energies (E), calculated using the Kissinger method are also given in these tables.

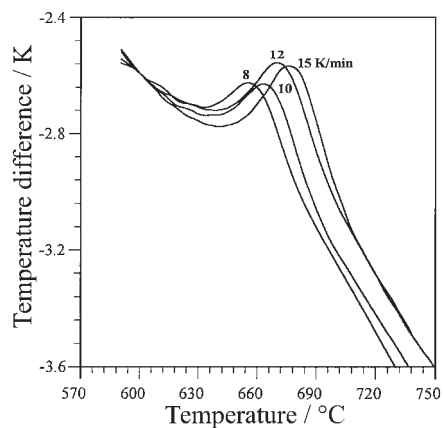


Fig. 1 DTA curves of ZnFe₂O₄ formation obtained with the ferric yellow Hrušov at various heating rates

As the ICTA Standardization Commission recommends, in the interest of consistency of the results, to quote only the data obtained at a heating rate of 10 K min^{-1} , the temperatures corresponding to this heating rate are emphasized, which facilitates also comparing the pigments with respect to their reactivities.

Table 1 Characteristic temperatures, peak areas, and activation energies evaluated for the ferric oxides heated at individual rates

$\beta/\text{K min}^{-1}$	$T_{\text{ons1}}/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_{\text{ons2}}/^\circ\text{C}$	$P/\text{K s mg}^{-1}$	$E/\text{kJ mol}^{-1}$
Ferric red TP 303; mass 400 mg					
8	747.5	782.5	819.7	-0.175	282±35
10	746.4	786.7	830.6	-0.270	
12	752.2	795.3	835.4	-0.213	
15	756.2	800.9	838.8	-0.229	
Ferric red FB 110; mass 500 mg					
8	831.8	857.3	881.7	-0.083	456±33
10	835.4	861.3	889.0	-0.089	
12	843.8	869	894.1	-0.083	
15	844.6	871.3	897.9	-0.075	
Ferric red FB 130; mass 500 mg					
8	840.1	867.8	900.0	-0.122	475±32
10	844.8	873.4	899.5	-0.092	
12	844.7	876.4	901.7	-0.089	
15	851.6	881.9	907.1	-0.079	
Ferric yellow Hrušov; mass 400 mg					
8	630.0	659.0	685.5	-0.200	205±4
10	635.4	666.5	694.1	-0.202	
12	639.6	672.6	702.1	-0.211	
15	646.1	680.0	711.5	-0.209	
Ferric yellow B 920; mass 300 mg					
8	654.8	684.0	713.0	-0.267	231±25
10	665.7	692.7	725.6	-0.222	
12	667.2	693.7	728.1	-0.196	
15	672.8	703.9	733.0	-0.216	

Tables 1 and 2 show that the temperature at which individual reactions run and the appropriate activation energies are different. In case of different chromic oxides the differences in reactivity are not so high. The highest reactivity is shown by the Bayer GX Cr_2O_3 , which exhibits in comparison to other pigments, the largest peak surface and the lowest activation energy. It can be said that the reaction between ZnO and Cr_2O_3 runs, in

our case, in a temperature range of 630–780°C. With respect to their reactivities the Cr₂O₃ pigments show the order as follows: Cr₂O₃ Bayer GX > Cr₂O₃ Acrox > Cr₂O₃ p.a.

Table 2 Characteristic temperatures, peak areas, and activation energies evaluated for the chromic oxides heated at individual rates

$\beta/\text{K min}^{-1}$	$T_{\text{ons1}}/^\circ\text{C}$	$T_{\text{p}}/^\circ\text{C}$	$T_{\text{ons2}}/^\circ\text{C}$	$P/\text{K s mg}^{-1}$	$E/\text{kJ mol}^{-1}$
Cr ₂ O ₃ Bayer; mass 600 mg					
8	613.9	685.2	768.0	-0.768	128±2.5
10	626.1	704.5	780.7	-0.685	
12	631.3	707.0	791.1	-0.778	
14	638.9	715.9	797.3	-0.742	
Cr ₂ O ₃ Acrox; mass 600 mg					
8	647.3	690.8	731.8	-0.253	158±12
10	654.9	702.2	745.4	-0.254	
12	661.7	710.8	753.9	-0.250	
14	664.7	715.6	758.8	-0.235	
Cr ₂ O ₃ p. a.; mass 600 mg					
8	675.9	727.5	763.5	-0.147	157±20
10	695.7	732.3	776.9	-0.097	
12	705.7	749.4	788.9	-0.105	
14	699.7	753.9	794.8	-0.129	

The ferric pigments show distinct differences in reactivity. The extrapolated onset temperatures (T_{ons1}) differ in case of interest by as high as 200°C. The ferric yellows are much more reactive than the ferric reds. The lowest reactivities are shown by the ferric FB 110 and FB 130 reds, the activation energy is in this case high (as 475 kJ mol⁻¹), and the peak areas are comparatively low. The different reactivities of ferric reds start with different ways of preparation thereof. The ferric red TP 303 is prepared via the thermal decomposition of iron(II) sulfate heptahydrate (green vitriol), whereas the ferric reds FB 110 and FB 130 are by-products received in the aniline production. On the contrary to chromic oxides it is not possible to define precisely the running reaction range, as the range is heavily affected by the ferric pigment used.

Table 3 Changes in the specific surface $S_o/\text{m}^2/\text{g}^{-1}$ of ferric yellows in dependence on the firing temperature

Pigment	Non-calcinated	400°C/1 h	500°C/1h	600°C/2 h	800°C/2 h
Ferric yellow Hrušov	16.21	61.36	18.54	15.9	3.83
Ferric yellow B 920	16.49	73.7	19.35	13.55	6.08

The reactivities of ferric yellows with respect to those of ferric reds are given by the Hedvall effect. On heating the ferric yellows lose their crystal water and increase

sharply their specific surface. The change of specific surface given as depending on overburning temperature for the ferric yellows is shown in Table 3. The data show that in the region of dehydration the specific surface grows to a 4-fold of this original value. With increases in temperature of overburning the specific surface drops. It was found that reactivity also (evaluated by the reaction of various overburnt ferric yellows with ZnO) drops with increase in the overburning temperature.

From the reactivity point of view the ferric pigments can be ordered as follows: ferric yellow Hrušov > ferric yellow B 920 > ferric red TP 303 > ferric red FB 110 > ferric red FB 130.

By comparing the reactivities of chromic oxides and ferric pigments we can find that ferric yellows exhibit approximately the same level of reactivity as chromic oxides, which, however, are characterized by a lower value of activation energy. The least reactivities are shown by the ferric reds. It can also be observed that most of the pigments react in a range of 80–110°C, only the chromic oxide of Bayer show a difference between the reaction onset and end temperature as high as 180°C. The activation energy values found for Cr₂O₃ vary in a range of 130–160 kJ mol⁻¹, whereas those for ferric pigments are positioned in a range of 200–475 kJ mol⁻¹.

The activation energies for some pigments were determined also by the method of isothermal kinetics applied to measurements performed at 3 various firing temperatures for reaction mixtures (the curves were determined on the basis of the degree of conversion in fired reaction mixtures found by the chemical analysis methods). The values thus determined are given in Table 4. It can be seen that the appropriate activation energy values are lower, but the sequence of reactivities found for the pigments is the same as that obtained by the DTA measurements. An advantage of determining the activation energies by the DTA procedure consists in independence of their determination. In case of isothermal kinetic measurements of the activation energies they are determined by calculation of the rate constants bound to certain mathematical models [24].

Table 4 Activation energy values determined by the isothermal measurement method

Pigment	Cr ₂ O ₃ Bayer GX	Ferric yellow Hrušov	Ferric red TP 303	Ferric red FB 130
<i>E</i> /kJ mol ⁻¹	87.05	138.85	181.51	330.40

The DTA curves were converted to the $y(\alpha)$ and $z(\alpha)$ dependences using the formulas given above. An example of such a dependence is reproduced for ferric yellow Hrušov in Fig. 2, wherein the points correspond to various heating rates. It is evident that both the functions do not depend on the heating rates and in both cases it is possible to determine well defined maxima: $a_M=0.363\pm 0.052$ and $\alpha_p^\infty=0.544\pm 0.035$. If we compare these values to an earlier reported schema [19] then it is possible to conclude that the processes of interest can be approximated using a two – parameter model SB (m, n), which is sometimes designated as an autocatalytic one (this model represents the so-called empirical kinetic model formulated as $f(\alpha)=\alpha^m(1-\alpha)^n$ [23, 25]. The same conclusion can be taken also in case of other pigments being investigated. Table 5 contains the kinetic parameters calculated for the model concerned [20] and the

pre-exponential factor. Values for pigments of interest and individual heating rates. For the respective calculations the activation energy values given in Tables 1 and 2 were used.

Table 5 Kinetic parameters for the pigments of interest; the averaged values are given in the form of $\bar{x} \pm s_x$

$\beta/\text{K min}^{-1}$	m	n	$\ln A$	$\beta/\text{K min}^{-1}$	m	n	$\ln A$
Ferric red TP 303; $E=281 \text{ kJ mol}^{-1}$				Ferric red FB 110; $E=456 \text{ kJ mol}^{-1}$			
8	0.39	0.96	27.72	8	0.48	1.14	44.70
10	0.47	1.39	27.50	10	0.44	1.20	44.03
12	0.43	1.26	27.31	12	0.47	1.10	44.16
15	0.54	1.25	27.46	15	0.53	1.01	44.33
Average	0.46 ± 0.06	1.30 ± 0.08	27.50 ± 0.17	Average	0.48 ± 0.04	1.11 ± 0.08	44.31 ± 0.29
Ferric red FB 130; $E=475 \text{ kJ mol}^{-1}$				Ferric yellow; $E=205 \text{ kJ mol}^{-1}$			
8	0.30	1.02	45.54	8	0.50	0.92	21.93
10	0.42	0.97	45.63	10	0.55	0.95	21.93
12	0.28	0.95	45.50	12	0.67	0.99	22.15
15	0.47	1.15	45.80	15	0.56	1.14	21.85
Average	0.38 ± 0.09	1.02 ± 0.09	45.6 ± 0.13	Average	0.57 ± 0.07	1.00 ± 0.1	21.97 ± 0.13
Ferric yellow B 920; $E=231 \text{ kJ mol}^{-1}$				Cr_2O_3 Bayer GX; $E=128 \text{ kJ mol}^{-1}$			
8	0.56	1.28	24.67	8	0.25	1.00	10.45
10	0.49	1.19	24.56	10	0.23	0.88	10.38
12	0.44	1.15	24.68	12	0.29	1.08	10.44
15	0.53	1.23	24.62	14	0.28	1.02	10.43
Average	0.51 ± 0.05	1.21 ± 0.06	24.63 ± 0.06	Average	0.26 ± 0.03	1.00 ± 0.08	10.43 ± 0.03
Cr_2O_3 Acrox; $E=158 \text{ kJ mol}^{-1}$				Cr_2O_3 p. a.; $E=157 \text{ kJ mol}^{-1}$			
8	0.47	0.88	14.61	8	0.54	0.88	13.71
10	0.31	0.88	14.47	10	0.53	0.84	16.36
12	0.54	1.05	14.74	12	0.30	0.69	13.52
14	0.37	0.87	14.67	14	0.43	0.84	13.73
Average	0.42 ± 0.1	0.88 ± 0.01	14.62 ± 0.11	Average	0.50 ± 0.06	0.85 ± 0.02	13.65 ± 0.12

Table 5 shows clearly that the changes in magnitude of kinetic parameters induced by a varying heating velocity fluctuate, in most cases, in a range of 10–15%. Figure 3 indicates a comparison between the experimental DTA curve (dotted line) and the curve calculated [19] for the kinetic parameters corresponding to the individual heating rates (solid lines) for ferric yellow Hrušov. The agreement between both dependences is evi-

dently good. Also for other pigments a good agreement was achieved between the experimental and theoretical curves, the ferric yellow B 920 shows a rather evident discrepancy only between the two curves. In paper [19] the kinetic parameters given by the DSC procedure were compared to their counterparts determined by the DTA measurements, giving a conclusion that the DTA measurements are loaded by a little larger relative error. Despite to this we can conclude that the DTA measurements can also give usable results for describing the kinetics of the process of interest.

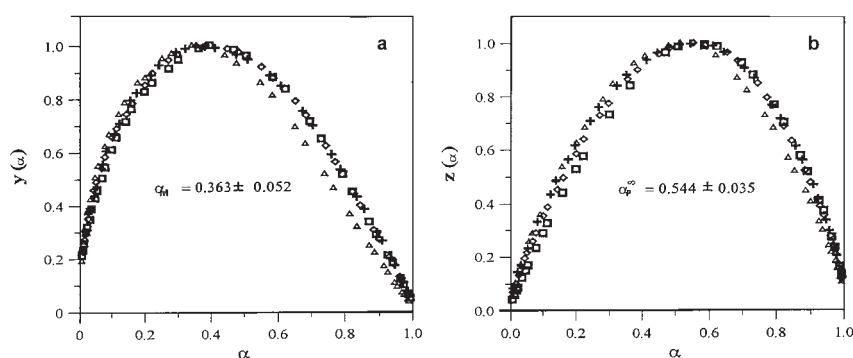


Fig. 2 Normalized $y(\alpha)$ function (a) and $z(\alpha)$ function (b) for the ferric yellow; The heating rates are designated by symbols as follows: + – 8; \diamond – 10; \square – 12 and Δ – 15 K min⁻¹; The points were obtained by transformations of DTA data

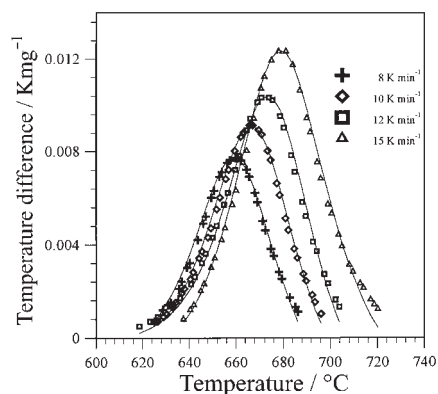
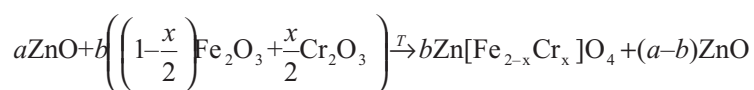


Fig. 3 Experimental (dotted) lines and calculated (solid) lines for the ferric yellow Hrušov at various heating rates

With respect to the fact that the SB model can be characterized as a more or less general one other kinetic models [19] (such as JMA(n), D2, D3, or D4) were also tested. Nevertheless a much worse agreement between the experimental and theoretical curves was achieved (in case of the D2, D3, and D4 models the courses of both curves showed to be quite different).

Conclusions

The methods of thermal analysis provide very useful information about the 'reactivity' of the starting materials for synthesis of the spinel like compounds, esp. for producing of mixed spinel type pigments. Considering e.g. the simplest three component, commercially produced ceramic pigment Zn-Fe-Cr type we can write formally the following chemical equation for its synthesis:



The degree of conversion (α) determined by means of chemical analysis of unreacted zinc oxide was usually α 0.98–0.99. The formal chemical equation may be understood as two parallel reactions for synthesis of ZnFe_2O_4 and ZnCr_2O_4 spinel compounds which are mutually soluble. Therefore the 'reactivities' of ferric and chromic oxides may predetermine and influence the relation of ferric and chromic ions in that mixed spinel and therefore the resulting pigments properties, e.g. the hue of brown colour too.

Experimentally it was proved [5, 27, 28] that choosing the source of Fe_2O_3 higher reactivity leads to mild (but visible) shift of the colour reddish brown hue in this pigment. On the contrary Fe_2O_3 annealed at higher temperature and therefore lower reactivity causes the colour shift in the opposite direction.

This is the main reason for the need of reactivity measurements of individual raw material (reactants), esp. when one of the reactants must be changed (another sort of raw material). For this evaluation of reactivity there may be used methods of TA (DTA, DSC, conductometric or dilatometric TA), the change of reactivity was evaluated according to the temperature range of reaction, or if it is needed, via the value of the temperature of reaction start or the value of activation energy.

Via following the non-isothermal kinetics of formation of the spinel-like compounds it was found that the formation kinetics can be best described by the general kinetic model SB(m, n). For other kinetic models (diffusion, nucleous...) no agreement was achieved between the experimental and derived master DTA curves.

Appendix

In this paper the method of separate determining of activation energy E is used, through analysing more TA curves when treated at various rates of heating β (method after Kissinger). To identify the suitable kinetic model there were two new functions $y(\alpha)$ and $z(\alpha)$ [29–31] defined. These functions can be calculated simply from the experimental data and they are close connected with those kinetic models.

The Eq. (4) formulates the kinetic model through the function $f(\alpha)$:

$$f(\alpha) = \frac{\Phi}{\Delta HA} e^x \quad (4)$$

and this one may be combined with the Eq. (5) of integral function $g(\alpha)$:

$$g(\alpha) = \frac{AE}{\beta R} e^{-x} \frac{\pi(x)}{x} \quad (5)$$

The product of these two functions is:

$$f(\alpha)g(\alpha) = \frac{\Phi}{\beta \Delta H} [\pi(x)T] \quad (6)$$

When using the Doyle's approximation of the so-called temperature integral $\pi(x) \approx 1/x$ it is evident that Málek's newly established function $z(\alpha)$ as a product of two functions $f(\alpha)$ and $g(\alpha)$ simply available from experiments:

$$z(\alpha) = f(\alpha)g(\alpha) \approx \Phi T^2 \quad (7)$$

From derived form $z'(\alpha)$ it is possible to find the maximum of this function and the appropriate value of α_p^∞ . The individual kinetic model, respectively a group of models, are then classified after the value α_p^∞ . The function $z'(\alpha)$ is practically independent of the value of activation energy. The determining of the suitable kinetic model and kinetic exponents enables the second function $y(\alpha)$. The expression of this function consist in a small rearrangement of the Eq. (1):

$$y(\alpha) = \Phi e^x = \Delta H A f(\alpha) \quad (8)$$

When knowing the value E , contained in $x = E/RT$, the value of $y(\alpha)$ can be simply calculated. To find the shape of $y(\alpha)$ and the value of maximum α_M the derived $y'(\alpha)$ is established and equalized to zero ($y'(\alpha) = 0$). From Eq. (8) it is evident that the shape of $y(\alpha)$ function is significantly affected by the value of E . Therefore this one must be determined with the uppermost precision.

Particular kinetic models, resp. types of models, differ in the course of these functions and in values of α_p^∞ and α_M . The diagram of the kinetic model determinations is described more in details in [30, 31].

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References

- 1 W. Büchner and R. Schliebs, Industrielle Anorganische Chemie, 2. Auflage, VHC Verlagsgesellschaft mbH, Weinheim 1986, p. 400.
- 2 Z. Šolc and M. Trojan, Sklář a keramik, 39 (1989) 16.
- 3 A. Kalendová, J. Šnupárek and P. Kalenda, Dyes and Pigments, 30 (1996) 129.
- 4 A. Kalendová and P. Kalenda, Polymers Paint Colour Journal, 184 (1994) 570.
- 5 Z. Šolc, M. Trojan and M. Pokorný, Silikáty, 29 (1985) 351.
- 6 G. A. Kolta, S. Z. El-Tawil and A. A. Ibrahim, Thermochim. Acta, 36 (1980) 359.
- 7 F. Paulik, Special Trends in Thermal Analysis, Wiley, Chichester 1995, p. 140.
- 8 V. Balek, Silikáty, 26 (1984) 147.
- 9 Z. Šolc, O. Pavlíček, M. Trojan and Z. Šmejkal, Thermochim. Acta, 190 (1991) 43.
- 10 J. Guilissen and P. J. Van Ryselberghe, Elektrochem. Soc., 59 (1931) 95.
- 11 J. F. Duncan and D. J. Stewart, J. Trans. Far. Soc., 63 (1967) 1031.
- 12 W. P. Kingery, Kinetics of High Temperature processes, Wiley, Massachussets 1959, p. 243.
- 13 T. Ishii, R. Furuichi and Y. Hara, J. Thermal Anal., 11 (1977) 71.

- 14 K. Meyer, Fiziko-Chimičeskaja Kristalografia, Metalurgia, Moskva, Russian 1972, p. 434.
- 15 R. Furuichi, S. Nakamo, S. Shimada and T. Ishii, Solid States Ionics, 63–65 (1993) 195.
- 16 J. Šubrt and J. Tláškal, Solid States Ionics, 63–65 (1993) 110.
- 17 M. Ueda, S. Shimada and M. Inagaki, Solid States Ionics, 63–65 (1993) 154.
- 18 B. Boyanov and I. Boyanova, Nauchni Tr. – Plodivski Univ., 23 (1985) 55; Chem. Abstr., 108 (1988) 119 814 g.
- 19 J. Málek and V. Smrčka, Thermochim. Acta, 186 (1991) 153.
- 20 J. Málek, Thermochim. Acta, 200 (1992) 257.
- 21 J. Málek and J. M. Criado, Thermochim. Acta, 236 (1994) 187.
- 22 J. Šesták, Thermophysical Properties of Solids, Elsevier, Amsterdam 1984.
- 23 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
- 24 S. F. Hulbert, J. Brit. Ceram. Soc., 1 (1970) 11.
- 25 J. Málek and J. M. Criado, Thermochim. Acta, 175 (1991) 305.
- 26 N. Koga, J. Šesták and J. Málek, Thermochim. Acta, 188 (1991) 333.
- 27 Z. Šolc and M. Trojan, J. Thermal Anal., 43 (1995) 69.
- 28 T. Konvička, Doctor Thesis, University of Pardubice, 1997.
- 29 J. Málek, Thermochim. Acta, 267 (1995) 61.
- 30 S. Montserrat and J. Málek, Thermochim. Acta, 228 (1993) 47.
- 31 J. Málek, J. Šesták, F. Rouquerol, J. Rouquerol, J. M. Criado and A. Ortega, J. Thermal Anal., 38 (1992) 71.