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APPLICATION OF NEURAL NETWORKS IN ANALYSIS OF THERMAL DECOMPOSITION OF $CoSO_4 \cdot 7H_2O$

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Abstract

Thermal decomposition of $CoSO_4 \cdot 7H_2O$ was investigated by simultaneous DTA-TG techniques and XRD method. Neural networks were used for DTA-TG curves analysis. Additionally, the network architecture (GRNN - Generalized Regression Neural Networks) and its statistical parameters were calculated. This method permits to generate DTA-TG curves without using kinetic models.

Keywords: $CoSO_4 \cdot 7H_2O$ thermal decomposition, DTA-TG methods, neural networks

Introduction

Kinetics of thermal decomposition processes of solids in the case of conventional methods is described by the equation:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{1}$$

where: α – degree of conversion, t – time, $f(\alpha)$ – function dependent of kinetic model for given reaction, $k(T)$ – rate constant of the reaction.

Kinetic constant of the reaction is expressed by Arrhenius equation and each stage of the reaction is treated as an independent reaction. After determining the $f(\alpha)$ function on the base of experimental data, a detailed formula of kinetic equation is obtained for each stage. About forty kinetic models are known based on various assumptions concerning the process mechanism [1]. Present discussions concern also being justifiable of the classic kinetics methods for the description of thermal decomposition processes of solids as well as the accuracy of obtained results [2–6]. The application of conventional methods requires a separate distinguishing of individual process stages and next their describing by complex expressions. In this work neural networks were applied for the description of cobalt(II) sulfate(VI) hydrate decomposition. Such networks enable a description of given process without a necessity of dividing it into stages, they are easy to handle and result in a very good accuracy of approximating the experimental data.

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Experimental

For DTA-TG investigations $CoSO_4 \cdot 7H_2O$ was used after obtaining it as a result of a slow crystallisation from a saturated solution of $CoSO_4$. The solution was prepared using $CoSO_4 \cdot nH_2O$ (pure, product of POCh Gliwice). The obtained crystals of $CoSO_4 \cdot 7H_2O$ were dried in acetone and ground in an agate mortar. The DTA-TG measurements were carried out applying the apparatus SDT 2960 of TA Instruments. They were performed in air atmosphere (air flow – ca. 100 ml min^{-1}) with the use of open corundum crucibles and portion masses of $CoSO_4 \cdot 7H_2O$ within the 21–37 mg range. DTA-TG studies were made at the following heating rates: 2, 4, 6, 8 and 10 K min^{-1}. For each heating rate three, independent DTA-TG measurements were carried out. For all heating rates a very good reproducibility of experimental data was obtained. In order to establish some, intermediate and final solid products of $CoSO_4 \cdot 7H_2O$ decomposition, separate samples of this salt were heated in air atmosphere for 4 h, at temperatures chosen on the base of the TG curves, i. e. at 400, 800 and 1000ºC. On completion of heating the samples were rapidly cooled to ambient temperature. Such obtained preparations were subjected to XRD examination. These investigations were carried out by means of DRON-3 diffractometer, applying the radiation CoK_α (λ=0.179021 nm).

For calculations the program Statistica Neural Network [7] was used. In this program the neural network is constructed by means of the tool IPS (Intelligent Problem Solver). After completion of the calculations the IPS creator establishes a set of networks best fitted to given problem, gives the number of variables taken into account and the accuracy of calculations. Quality of a network in the STNN program is assessed on the base of the indicators: Data Mean – average value of the target output variable; Data S.D. – standard deviation of the target output variable; Error Mean – average error (residual between target and actual output values) of the output variable; Abs.E. Mean – average absolute error (difference between target and actual output values) of the output variable; Error S.D. – standard deviation of errors for the output variable; S.D. Ratio – determined as the error divided by data standard deviation ratio; Correlation – the standard Pearson-R correlation coefficient between the target and actual output values. The indicators describing the quality of the network are determined independently for the sets: training Tr, verification Ve and testing Te. While estimating given network mainly the last two indicators were considered.

Results and discussion

Figure 1 presents experimental DTA and TG curves recorded for the heating rate of 10 K min^{-1}. On the basis of the quantitative results obtained from the thermogravimetric investigations (Table 1.) and literature information about a dehydration of sulfates(VI) of *d*-elements [8–13], the following mechanism of dehydration could be proposed:

I $$CoSO_4 \cdot 7H_2O_{(s)} = CoSO_4 \cdot 6H_2O_{(s)} + H_2O_{(g)} \quad (2)$$

incongruent melting $$CoSO_4 \cdot 7H_2O_{(s)} \leftrightarrows CoSO_4 \cdot 6H_2O_{(s)} + L_{(sat)} \quad (3)$$

Table 1 Temperature ranges of DTA peaks, minima of DTA peaks and mass losses recorded on TG curves obtained for $CoSO_4 \cdot 7H_2O$

Stage	Heating rate/ K min^{-1}	Temperature range of DTA peaks/K	Minimum of DTA peaks/K	Experimental mass losses/mass%	Theoretical mass losses/mass%
	2	296–319	307	5.96	
	4	299–328	311	6.42	
I	6	295–335	319	5.81	6.41
	8	296–338	319	6.05	
	10	308–335	322	5.78	
	2	327–373	351	31.86	
	4	332–391	359	32.26	
II	6	339–405	369	31.96	32.04
	8	341–408	372	32.08	
	10	336–422	369	32.17	
	2	502–568	536	6.89	
	4	504–578	550	7.29	
III	6	515–597	566	7.30	6.41
	8	517–596	562	6.50	
	10	520–623	569	7.27	
	2	950–1082	1076	26.53	
	4	975–1107	1098	26.78	
IV	6	993–1133	1116	26.80	26.58
	8	997–1132	1119	26.61	
	10	1008–1136	1119	26.76	
	2	1175–1194	1186	1.92	
	4	1179–1196	1190	2.00	
V	6	1179–1202	1191	1.96	1.90
	8	1180–1202	1191	1.98	
	10	1180–1204	1191	1.99	

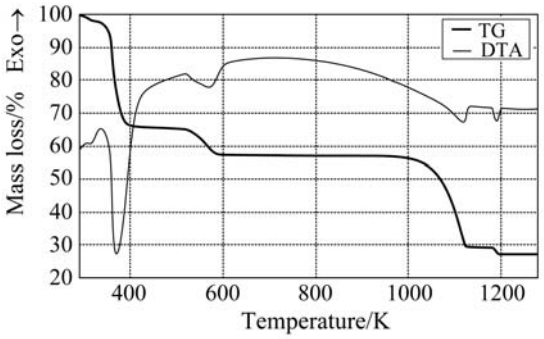

Fig. 1 Experimental DTA and TG curves recorded for the heating rate of 10 K min^{-1}

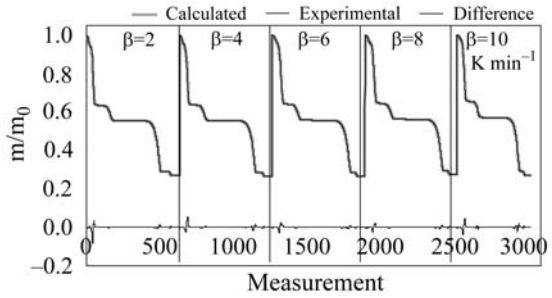

Fig. 2 Comparison of calculated and experimental TG curves

isothermal boiling $L_{(sat)} \rightarrow CoSO_4 \cdot 6H_2O_{(s)} + H_2O_{(g)}$ (4)

II $CoSO_4 \cdot 6H_2O_{(s)} = CoSO_4 \cdot H_2O_{(s)} + 5H_2O_{(g)}$ (5)

III $CoSO_4 \cdot H_2O_{(s)} = CoSO_{4(s)} + H_2O_{(g)}$ (6)

On the base of the mass loss observed on the TG curves and presented in Table 1, XRD investigations and literature information [14–16] desulphurization can be distinguished:

IV $3CoSO_{4(s)} = Co_3O_{4(s)} + 3SO_{2(g)} + O_{2(g)}$ (7)

V $Co_3O_{4(s)} = 3CoO_{(s)} + 1/2O_{2(g)}$ (8)

On the ground of XRD investigations, the solid products obtained after the third, fourth and fifth were determined. For description of the course of TG and DTA curves applying the neural networks, independent variables were temperature and heating rate, whereas a dependent variable was reduced mass m/m_0 (TG curves) and in the case of DTA curves – differential of temperature with respect to time. The results of TG and DTA measurements formed two separate sets of data. For the TG data set the network GRNN 2/1515 was selected (two independent variables and 1515 hidden neurones) of the following parameter values: S.D. Ratio for the set Tr 0.033; for the set Ve 0.041; for the set Te 0.041, correlation coefficient for all sets 0.99915. Fig-

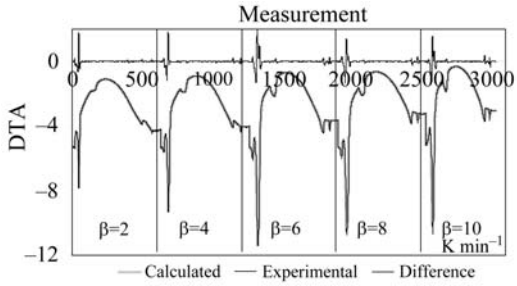

Fig. 3 Comparison of calculated and experimental DTA curves

ure 2 presents a comparison of the calculated TG curves with the experimental ones. Lower plot in Fig. 2 shows a difference between these curves. The obtained result indicates that by one neurone model all curves were described obtained at various heating rates and various masses of sample portions.

In a similar way the set of data concerning the DTA curves was worked out. In this case the network GRNN 2/1515 was also selected, for which the following values of parameters were obtained: S.D. Ratio for the set Tr 0.113; for the set Ve 0.139; for the set Te 0.121, correlation coefficient; 0.9937; 0.9905 and 0.9931, respectively. Figure 3 presents the calculated and experimentally determined DTA curves. Upper plot in this figure shows a difference between the curves. As it can be seen from Fig. 3, also in this case a very good accuracy of approximating the experimental data was attained.

Conclusions

The present study reports results of research conducted by DTA-TG methods for $CoSO_4 \cdot 7H_2O$. Mechanism of decomposition has been established for this salt on the base of TG and XRD investigations. This enabled determining the intermediate and final solid products of decomposition of cobalt(II) sulfate(VI) hydrate. Neural networks were applied here to describe the course of $CoSO_4 \cdot 7H_2O$ thermal decomposition. It has been established that the best approximation of the experimental curves TG and DTA is attained by applying the same neurone model GRNN 2/1515 for description of their shape. Application of neural networks makes possible obtaining very good reproducibility of DTA-TG experimental data.

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