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COMPUTER-AIDED THERMOGRAVIMETRIC DETERMINATION OF KINETIC PARAMETERS OF CALCINATION OF $BeSO_4 \cdot 4\ H_2O$

Gernot Braun [x], Heinz Roßbach, Heiner Herberg, Karin Henkel,
Central Institute for Nuclear Research Rossendorf, GDR

ABSTRACT

The multistage thermal decomposition of $BeSO_4 \cdot 4\ H_2O$ is investigated by computer-aided simultaneous thermal analysis (TG, DTG, DTA) in dependence on the gas atmosphere. Using the thermogravimetric data the kinetic parameters activation energy, pre-exponential factor, and formal reaction order of some decomposition stages are calculated by different methods.

INTRODUCTION

Sinteractive, high-pure BeO-powder is a basic material for the carrier substances of the high thermal conductivity and electrical resistance in microelectronical structural elements of high power density. It can be produced by means of thermal decomposition of beryllium sulphate. The $BeSO_4$-hydrates crystallizing from their solutions by variable precipitation methods are differing in the number of the crystal water molecules and in their consistence according to preparation conditions. The thermal decomposition of these hydrates and consequently the properties of the BeO-powder are dependent on the conditions of their production and Calcination. The mechanism of the thermal decomposition of some $BeSO_4$-hydrates is qualitatively and quantitatively represented in its general course and in its influence by the gas atmosphere.

EXPERIMENTAL

The simultaneous thermal analysis (TG, DTG, DTA) is carried out in a Mettler thermoanalyzer TA-1 with a middle temperature range furnace, quartz gas flow tube, PtRh-Pt-crucible holder DTA-21, and Al_2O_3-crucible 0.03 cm^3 by dynamic heating with 4 K/min up to 800 °C (under N_2/H_2, 4 : 1) respectively 1000 or 1200 °C (under N_2/air dry or N_2/air moist, 1 : 1). The temperature is held at the maximum over 60 minutes, the stream velocity of the gas mixture is 5 l/h. Mass of the sample is 10 mg, reference material is Al_2O_3.

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Sample material: $BeSO_4 \cdot x\ H_2O$, produced by solving of BeO in half-concentrated H_2SO_4 and once or twice done precipitations of the sulphate from the solution, regulating the pH between < 1 and 2.5, by means of pouring into ice-cooled ethanol and following drying at 70 °C.

Data registration and -processing: Up to five selected signals of the thermoanalyzer are digitally registered and treated by means of a developed special amplifier device and a microcomputer MPS 4944 (based on Zilog 80), containing a hardware-ADC and a software control regime. The measured values are displayed on a TV-screen, printed out and also punched out on a tape for off-line coupling respectively directly transfered by means of a MPS-link to the mini-computer KRS 4201. The data processing algorithm of the KRS 4201 for the smoothing and differentation of the data is estimated and optimized by dialogue communication between operator and display. The optimized data and the results of the kinetic calculations are printed out.

Using the so treated thermogravimetric data the kinetic parameters activation energy, pre-exponential factor, and formal reaction order are calculated by the integral method according to Coats and Redfern /1/, the differential method according to Freeman and Caroll /2/, and the modified differential method /3/.

RESULTS AND DISCUSSION

Fundamental process of reaction:

$BeSO_4$-hydrates decompose in several endothermic steps (fig. 1). The dehydratation proceeds under separation of a mean value of 3.8 Mol H_2O. Above 500 °C BeO forms under SO_3-emission in a approximately exponential reaction. The following fundamental process of reaction is valid for all analysed samples in conformance with the literature /4 - 6/:

$$BeSO_4 \cdot 3.8\ H_2O \xrightarrow[95\ ^{o}C]{-\ 2.0\ H_2O} BeSO_4 \cdot 1.8\ H_2O \xrightarrow[178\ ^{o}C]{-\ 1.0\ H_2O}$$

$$BeSO_4 \cdot 0.8\ H_2O \xrightarrow[236\ ^{o}C]{-\ 0.8\ H_2O} BeSO_4 \xrightarrow[706\ ^{o}C]{-\ 1.0\ SO_3} BeO \quad .$$

The attached mean temperatures of the extrapolated onset T_e under the explained controlled temperature programme (validly for the decomposition under dry air) are indicated in the equation. The process of reaction is only unessentially influenced by the con-

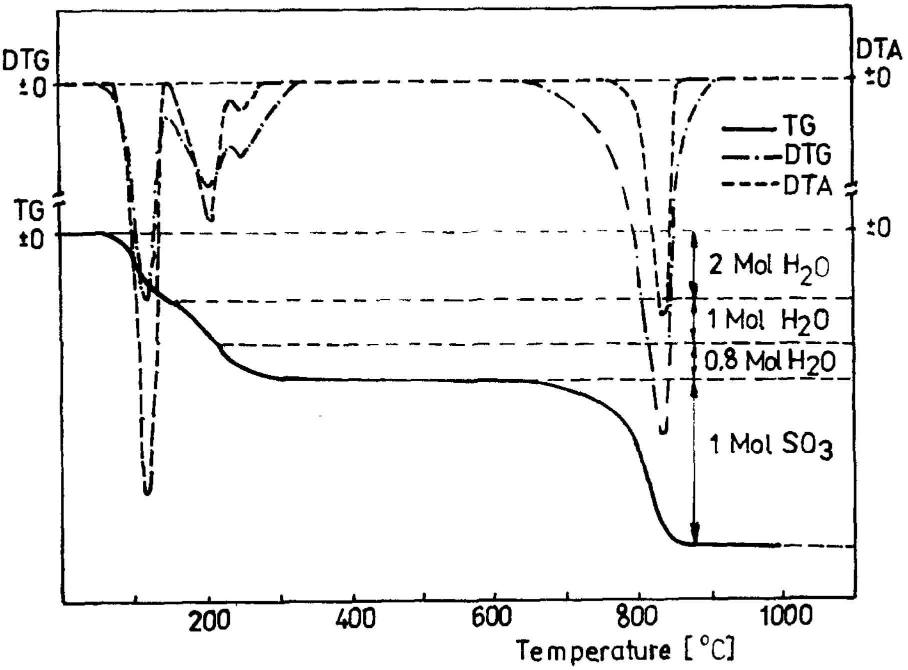

Fig. 1. TG-, DTG-, and DTA-curves of the fundamental process of the decomposition of $BeSO_4 \cdot x\ H_2O$

ditions of the preparation of the sulphates.

In the same way the gas atmosphere doesn't influence the fundamental process, however more or less distinctly various thermoanalytical test values especially of the 4th reaction. Under reducing N_2/H_2-atmosphere the SO_3-separation already begins on 40 up to 50 °C lower temperatures and finishes up to 100 °C lower. This acceleration of the reaction and this lowering of the onset temperature of the reaction are caused by the reducing effect of the H_2 on the SO_3 and therefore by the resultant displacement of the SO_3/SO_2-equilibrium. A higher partial pressure of steam of the air accelerates the sulphate emission by several samples.

Kinetic analysis:

The four decomposition reactions proceed to following general mechanism of the phase-boundary reaction:

$$\ln d\alpha/dT = \ln k_0/q - E/RT + n \ln (1 - \alpha) \quad .$$

A definite model separation isn't possible in any case because of the overlapping dehydratation steps and the long starting period of the SO_3-emission (see table 1). Different mechanisms are controlling the reaction rate within the total reaction interval of the 4th reaction. The model that exactly describes this reaction is dependent on the gas atmosphere (see table 2).

TABLE 1. Kinetic parameters of the four decomposition reactions under N_2/air dry (instance: $BeSO_4 \cdot 3.8\ H_2O$, pH< 1)

Reaction	n	E /kJ/Mol/	ln k_0 /min^{-1}/	Model equation (Initial differ.equat.)
1	1.2	150	47	$d\alpha/dt = k\ (1 - \alpha)^{3/2}$
2	0.9	119	30	$d\alpha/dt = k\ (1 - \alpha)^{3/2}$
3	0.7	211	48	$d\alpha/dt = k\ (1 - \alpha)^{2}$
4	0.4	187	19	$d\alpha/dt = k\ (1 - \alpha)^{1/2}$

TABLE 2. Mean kinetic parameters and laws for the 4th reaction in dependence on the gas atmosphere

Gas atmosphere	n	E /kJ/Mol/	ln k_0 /min^{-1}/	Mechanism / Model
N_2/air dry	0.6	195	20	phase-bound.reac. / 3
N_2/air moist	0.6	213	22	phase-bound.reac. / 3
N_2/H_2	1.0	252	29	phase-bound.reac. / 4

Under dry and moist air the SO_3-emission follows a phase-boundary model corresponding model equation 3 (in linearized form):

$$\ln(1 - \sqrt[3]{1-\alpha}) - \ln 1/3 - 2 \ln T = \ln k_0/q + \ln R/E - E/RT \quad ,$$

under N_2/H_2 corresponding model equation 4:

$$\ln[-\ln(1 - \alpha)] - 2 \ln T = \ln k_0/q + \ln R/E - E/RT \quad .$$

The reaction order and activation energy attain under N_2/H_2 maximum values. The qualitatively detected dependence of the SO_3-emission on the gas atmosphere using T_e and DTA is therefore quantitatively confirmed by means of kinetic analysis.

REFERENCES

1 A.W. Coats and J.P. Redfern, Nature 4 (1964) 88
2 E.S. Freeman and B. Caroll, Phys. Chem. 62 (1958) 394
3 S. Boy and K. Böhme, Thermochim. Acta 27 (1978) 390
4 I.J. Bear, Aust. J. Chem. 21 (1968) 21
5 D.R. Petersen et al., J. Phys. Chem. 68 (1964) 3057
6 S. Matsuda et al., Yogyo Kyokai-Shi 79 (1971) 351