

ISOTHERMAL INVESTIGATION OF DECOMPOSITION OF $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ - BaO_2 MIXTURES

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Abstract

Isothermal studies were conducted on mixtures of $\text{Fe}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in BaO_2 in molar ratios of $n=4, 2$ and 1 at temperatures of 573 and 1073 K, in a closed crucible, in air as gas medium. The solid products of decomposition were investigated by means of X-ray analysis, Mössbauer spectroscopy and electron spectroscopy.

The experiments revealed that the mechanism of the process is connected with the formation of different quantities of barium ferrites (BaFeO_3 , BaFe_2O_4 and $\text{BaFe}_{12}\text{O}_{19}$), as well as BaSO_4 and Fe_2O_3 , depending on the quantity of BaO_2 in the initial mixture, the partial pressure of the gas components and temperature. Differences were found in the mechanism of the process for the same mixtures under dynamic temperature conditions.

Keywords: barium ferrites, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ - BaO_2 mixtures, isothermal studies, Mössbauer spectroscopy, thermal decomposition, X-ray analysis

Introduction

Martinez [1, 2] and Pelovski [3, 4] have investigated possibilities of obtaining different barium ferrites such as BaFeO_3 , BaFe_2O_4 , Ba_2FeO_4 , Ba_3FeO_5 and $\text{BaFe}_{12}\text{O}_{19}$, during the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and BaO_2 . All their experiments were carried out under dynamic heating conditions. It has been established that the formation of ferrites in an $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ - BaO_2 system depends on the ratio of the initial reagents, the temperature, the heating conditions, and the partial pressures of the gaseous components, such as oxygen, water vapour, and SO_2/SO_3 . It has been proved that the main factor in the interaction is the release of atomic oxygen from BaO_2 and the strong oxidizing effect of peroxide ions.

The goal of this work was to investigate the interactions between $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and BaO_2 in mixtures with molar ratios $n=4, 2$ and 1 , in an oxidizing gaseous medium, in closed crucibles, at temperatures of 573 and 1073 K.

Investigation methods

The experiments were carried out under isothermal conditions for 60 min, in the laboratory set-up shown in Fig. 1. This installation for isothermal gravimetry includes an electric heating furnace with a thermoregulating system. The sensitive element for establishing mass losses is a molybdenum spiral, characterized by high

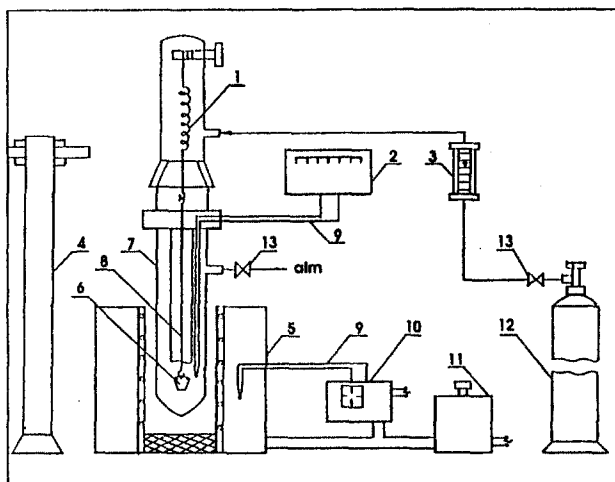


Fig. 1 Experimental set-up: 1 – spiral thermoscale; 2 – recording device; 3 – rotameter; 4 – cathetometer; 5 – electric heating furnace; 6 – crucible; 7 – reactor; 8 – platinum filament; 9 – thermocouples; 10 – thermoregulator; 11 – V-converter; 12 – gas mixture container; 13 – valves

elasticity and linear expansion. Mass changes of the samples are established in the elasticity range of the spiral through KM-6 cathetometer readings, on the basis of a preliminary calibration. Sample temperatures are measured with a platinum-rhodium thermocouple, connected to a 'Servogor-120' recording device. The sample mass was 3700 mg. Closed corundum crucibles were used, with an internal diameter of 10 mm and a height of 30 mm.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and BaO_2 were chemically pure for analysis. The content of basic substance in the BaO_2 was 95.07%. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dehydrated to $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ through preliminary heating at 353 K and $0.6 \cdot 10^{-5}$ Pa. The product contained 55.93% SO_4^{2-} , 34.57% Fe^{2+} and 9.50% crystallization water.

Decomposition end-products were analysed by X-ray diffraction, electron microscopy and Mössbauer spectroscopy.

X-ray analyses were carried out with a PHILIPS X-ray diffractometer with a monochromator, CuK_α radiation at 70 kV, 20 mA, $4 \cdot 10^2$ $1^\circ/\text{min}$, and 1 cm min^{-1} .

Electron microscopy pictures were taken with a PHILIPS EM 400 instrument at 60 kV, in the electron magnification range 11700–33000.

Mössbauer analyses were carried out with a standard Mössbauer spectrometer, under the constant acceleration of a radioactivity source (^{57}Co in Pd). The calibration of the rate scale is given in relation to $\alpha\text{-Fe}$.

Results and discussion

The experimental conditions for the isothermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ – BaO_2 mixtures through isothermal heating are given in accordance with the

results of the investigations of the mechanism of the process during dynamic heating [4]. Carrying out the experiments in closed crucibles diminishes the influence of gaseous-phase oxygen, and increases the influence of oxygen released by BaO₂ in the nascent state. The temperatures of 573 and 1073 K were chosen to lie in the two ranges where the reactions between FeSO₄·H₂O and BaO₂ proceed most intensively.

The results of the analyses of solid decomposition products are shown in Table 1 and Figs 2–8.

The thermal analysis and physico-chemical methods revealed some fundamental relations for the mechanism of the process in both the low-temperature and high-temperature ranges, depending on the experimental conditions.

$T=573$ K. The experiments prove the reactions at 573 K are connected with the dehydration of the last water molecule in the structure of FeSO₄·H₂O and the formation of FeSO₄·FeSO₄ is the basic phase in the end-products, especially at molar ratios of $n=4$ and 2, where FeSO₄·H₂O is in excess in the initial mixtures. FeO·HSO₄ was found as a product of partial oxidation of FeSO₄·H₂O. The quantity of Fe²⁺ in FeSO₄ form varies substantially for the different molar ratios: at $n=4$ it is 65%, and at $n=1$ it is 39% of the total Fe in the system. The quantity of Fe²⁺ in FeOHSO₄ form is relatively constant: 13 to 17% in the end-products.

The presence of BaO₂ in the initial mixtures determines the reactions of oxidation and formation of ferrites in the system, and physico-chemical methods prove the presence of BaFeO₃, BaFe₂O₄ and BaSO₄ in the decomposition end-products. X-ray and electron microscopy data (Figs 4 and 7) confirm that small-scale crystalline end-products were obtained. As compared with the large-scale crystalline

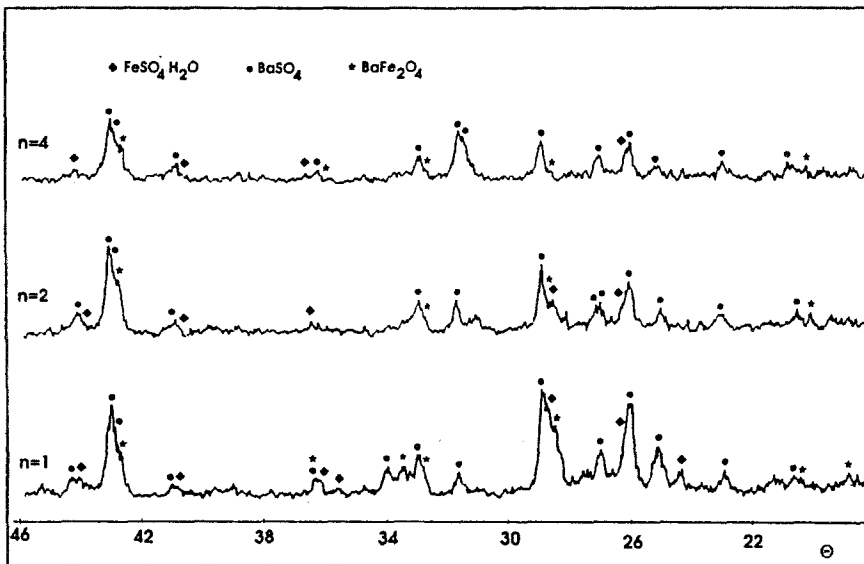


Fig. 2 Röntgenograms of end-products of thermal decomposition of FeSO₄·H₂O–BaO₂, $n=4$, 2 and 1, $T=573$ K, in closed crucibles and oxidizing gaseous medium

Table 1. Mössbauer spectroscopy and X-ray data on end-products of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ - BaO_2 mixtures

No.	T/K	n	Mass loss/%	Parameters		$H_{\text{eff}}/\text{kOe}$	Valence	Content of $\text{Fe}^{n+}/\%$	Identified phases by:	
				$\delta_{\text{is}}/\text{mm s}^{-1}$	$\Delta E_Q/\text{mm s}^{-1}$				Mössbauer spectroscopy	X-ray
1	573	4	9.2	1.10	2.75	-	Fe^{2+}	65	FeSO_4	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
				0.45	1.20	-	Fe^{3+}	17	FeOHSO_4	BaSO_4
				0.20	0.23	480	Fe^{3+}	10	BaFe_2O_4	BaFe_2O_4
				0.32	-	-	Fe^{3+}	8	BaFeO_3	
2	573	2	10.3	1.10	2.75	-	Fe^{2+}	52	FeSO_4	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
				0.20	0.23	480	Fe^{3+}	23	BaFe_2O_4	BaFe_2O_4
				0.40	1.25	-	Fe^{3+}	15	FeOHSO_4	BaSO_4
				0.32	-	-	Fe^{3+}	10	BaFeO_3	
3	573	1	8.9	1.10	2.75	-	Fe^{2+}	39	FeSO_4	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
				0.45	0.23	-	Fe^{3+}	26	$\text{BaFeO}_x; x=2.5-3$	BaSO_4
				0.20	0.23	480	Fe^{3+}	22	BaFe_2O_4	BaFe_2O_4
				0.40	1.20	-	Fe^{3+}	13	FeOHSO_4	
4	1073	4	36.4	0.30	0.44	516	Fe^{3+}	82	$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}_3, \text{BaSO}_4$
				0.30	0.40	480	Fe^{3+}	10	BaFe_2O_4	BaFe_2O_4
				0.30	0.40	480	Fe^{3+}	8	$\text{BaFe}_{12}\text{O}_{19}$	$\text{BaFe}_{12}\text{O}_{19}$
				0.30	0.44	516	Fe^{3+}	60	$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}_3, \text{BaSO}_4$
5	1073	2	23.0	0.30	0.40	480	Fe^{3+}	25	BaFe_2O_4	BaFe_2O_4
				0.30	0.40	480	Fe^{3+}	15	$\text{BaFe}_{12}\text{O}_{19}$	$\text{BaFe}_{12}\text{O}_{19}$
				0.30	0.44	516	Fe^{3+}	44	$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_2\text{O}_3, \text{BaSO}_4$
				0.30	0.40	480	Fe^{3+}	38	BaFe_2O_4	BaFe_2O_4
6	1073	1	15.1	0.30	0.40	480	Fe^{3+}	18	$\text{BaFe}_{12}\text{O}_{19}$	$\text{BaFe}_{12}\text{O}_{19}$
				0.30	0.40	480	Fe^{3+}	18	$\text{BaFe}_{12}\text{O}_{19}$	$\text{BaFe}_{12}\text{O}_{19}$

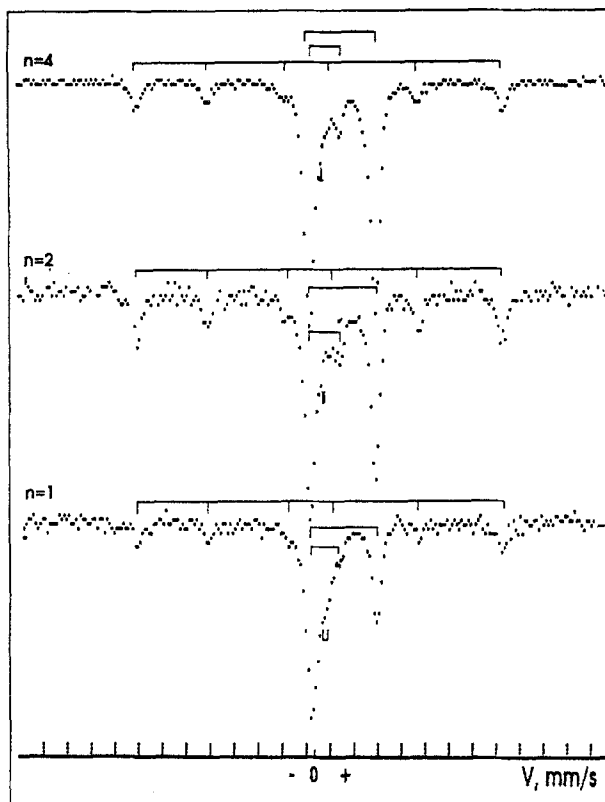


Fig. 3 Mössbauer spectra of end-products of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}-\text{BaO}_2$, $n=4, 2$ and 1 , $T=573$ K, in closed crucibles and oxidizing gaseous medium

structure of the initial FeSO_4 , the electron microscopy photographs show the presence of small crystals with strong agglomeration. This indicates high-intensity reactions, as a result of which the new phases obtained could not crystallize well.

$T=1073$ K. The thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}-\text{BaO}_2$ mixtures with $n=4-1$ at 1073 K is determined by the fact that the initial temperature is raised in a short period from 293 K. This determines $\alpha\text{-Fe}_2\text{O}_3$ as a basic phase at $n=4$ and 2 in the decomposition end-products (Table 1). Mössbauer spectroscopy and X-ray data prove the presence of BaFe_2O_4 , $\text{BaFe}_{12}\text{O}_{19}$ and BaSO_4 as well. Their quantities in the solid decomposition products increase with increase of the BaO_2 quantity in the initial mixture. A new kind of barium ferrite is found: $\text{BaFe}_{12}\text{O}_{19}$, which is not obtained at 573 K. The content of Fe^{3+} in the form of BaFe_2O_4 and $\text{BaFe}_{12}\text{O}_{19}$ in the decomposition end-products for all mixtures with $n=4-1$ increases from 10% at $n=4$ to 38% at $n=1$ for BaFe_2O_4 , and from 8 to 18% for $\text{BaFe}_{12}\text{O}_{19}$, and the data almost fully coincide with those obtained under dynamic heating conditions (Table 1) [4]. X-ray and electron microscopy data (Figs 5 and 8) confirm the formation of well-crystallized solid phases.

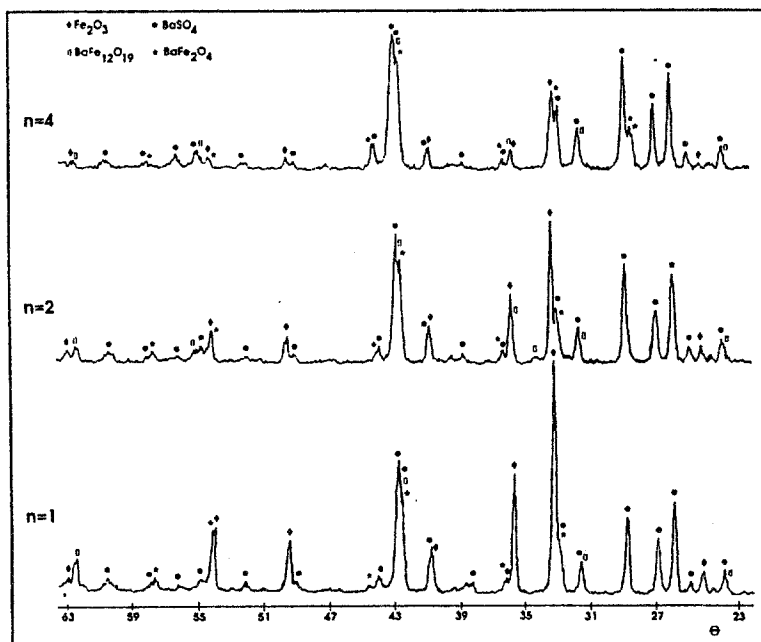
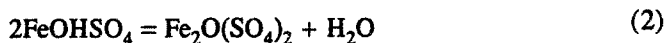


Fig. 4 Röntgenograms of end-products of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}-\text{BaO}_2$, $n=4, 2$ and 1 , $T=1073$ K, in closed crucibles and oxidizing gaseous medium

The experimental data permitted some suppositions concerning the most probable mechanism of the process of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}-\text{BaO}_2$ mixtures under isothermal heating conditions.

$\text{FeSO}_4 \cdot \text{H}_2\text{O}$. Besides the X-ray and electron spectroscopy data, an evaluation of the role of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ demands a consideration of the facts that at 573 and 1073 K the reaction gases were not let out from the reaction space during the experiments, and that the reaction space in the closed crucibles is comparatively small.

At 573 K, the main reaction is the dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ to FeSO_4 (Table 1, Figs 2 and 3). It is possible that part of the Fe^{2+} is oxidized to Fe^{3+} , in parallel with the dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ [5]. The Mössbauer spectroscopy data confirm the formation only of FeOHSO_4 , but not $\text{Fe}_2\text{O}(\text{SO}_4)_2$. Previous investigations proved that the formation of FeOHSO_4 and/or $\text{Fe}_2\text{O}(\text{SO}_4)_2$ necessitates certain temperatures and $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$ levels in the gaseous phase [5], while the equilibrium between the two sulphates is defined by the following reactions:



The formation of FeOHSO_4 is determined by the temperature conditions: at 573 K, FeOHSO_4 is a more stable phase than $\text{Fe}_2\text{O}(\text{SO}_4)_2$ [5]. The necessary con-

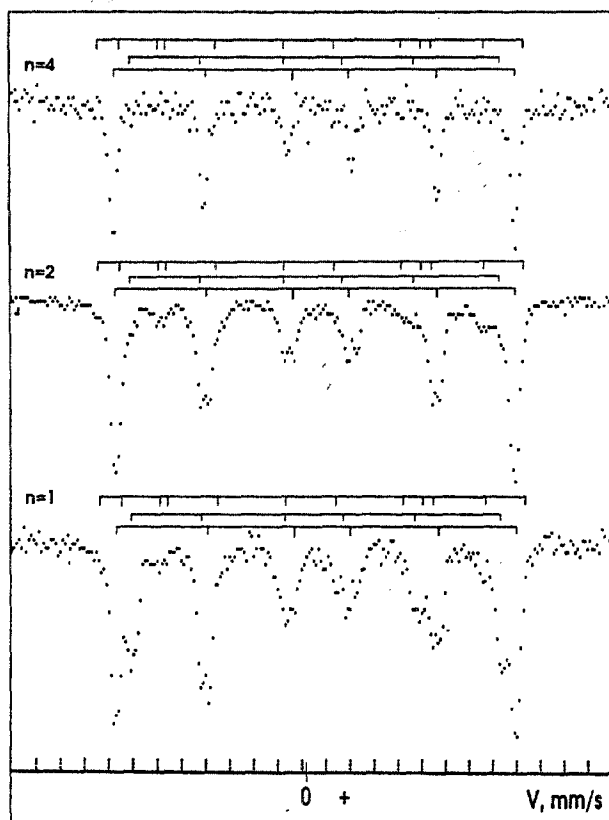


Fig. 5 Mössbauer spectra of end-products of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O} - \text{BaO}_2$, $n=4, 2$ and 1 , $T=1073$ K, in closed crucibles and oxidizing gaseous medium

tent of $P_{\text{H}_2\text{O}}$ is sustained by the dehydration process, and that of P_{O_2} by the release of atomic oxygen from the BaO_2 molecule. It is possible to assume that, with increase of the BaO_2 content of the initial mixture, the content of P_{O_2} also increases, which leads to the formation of greater quantities of FeOHSO_4 (and smaller quantities of FeSO_4) for $n=4-1$ (Table 1). The content of iron in the form of FeOHSO_4 remains relatively stable: 17% to 13% for $n=4-1$ (Table 1). Most probably, FeOHSO_4 is partly exhausted due to its participation in the formation of ferrites in the system. The established quantities are more likely to be the FeOHSO_4 remaining after these reactions. It is supposed that, of the different iron sulphates ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$, FeSO_4 and FeOHSO_4) FeOHSO_4 participates in the formation of barium ferrites. These suppositions are confirmed both by the measured mass losses in the system (Table 1) and by the fact that 573 K is the upper limit of the thermal stability range of FeOHSO_4 [4, 5]. At 573 K and in the presence of atomic oxygen, it is most probable that FeOHSO_4 interacts with BaO/BaO_2 as the least stable of the iron sulphates. Otherwise, $\text{Fe}_2\text{O}(\text{SO}_4)_2$ or $\text{Fe}_2(\text{SO}_4)_3$ should be obtained. Such phases were not found by physico-chemical methods.



Fig. 6 Electron microscopic photograph of initial $\text{FeSO}_4 \cdot \text{H}_2\text{O}$

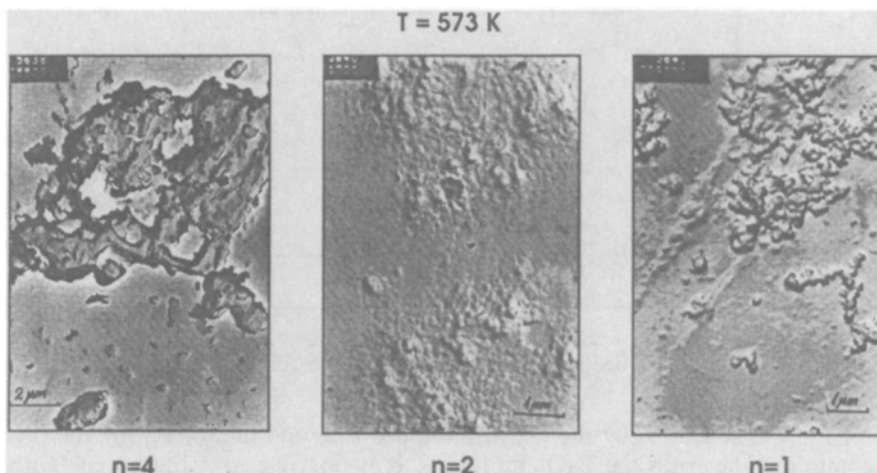
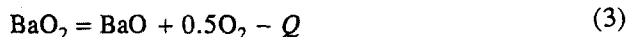


Fig. 7 Electron microscopic photographs of end-products of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O} - \text{BaO}_2$, $n=4$, 2 and 1, $T=573$ K, in closed crucibles and oxidizing gaseous medium

It is possible that at 1073 K the dehydration process proceeds more rapidly, without the formation of intermediate iron sulphates. Further, at 1073 K FeSO_4 is thermally unstable [5], and it starts to decompose to $\alpha\text{-Fe}_2\text{O}_3$. Physico-chemical analysis data confirm that, especially at $n=4$ and 2, $\alpha\text{-Fe}_2\text{O}_3$ is the main phase in the solid products of decomposition (Table 1, Figs 4 and 5).

BaO_2 . Unlike $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, BaO_2 is exhausted completely as a result of the interactions in the system, even at 573 K. BaO_2 starts to decompose and releases atomic oxygen in the following reaction:



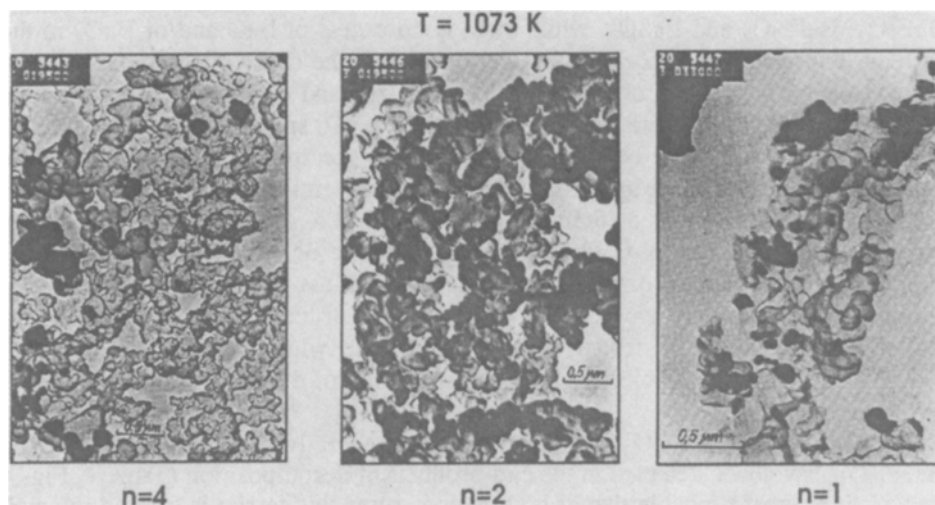


Fig. 8 Electron microscopic photographs of end-products of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O} - \text{BaO}_2$, $n=4, 2$ and 1 , $T=1073$ K, in closed crucibles and oxidizing gaseous medium

This process is speeded up by the presence of iron salts, which lowers the temperature of its decomposition considerably [4]. Due to its exceptional reactivity and strong oxidizing action, this atomic oxygen atom causes reactions which would be impossible under different conditions, such as the formation of some barium ferrites even at 573 K. These reactions are strongly exothermic and proceed very intensively [4]. The barium in the end-products after the decomposition of the initial mixture is distributed as BaO_2 and barium ferrites: BaFeO_3 , BaFe_2O_4 and $\text{BaFe}_{12}\text{O}_{19}$.

An increased content of BaO_2 in the initial mixture increases the intensity of the processes, as proved by the X-ray and electron microscopy data (Figs 2 and 7). The obtained end-products have a feebly marked crystalline structure and are almost fully X-ray amorphous.

Formation of ferrites. The possibility of ferrite formation is a basic characteristic in the interaction between FeSO_4 and BaO_2 . Previous investigations of the same system have proved that ferrite formation is provoked by the released atomic oxygen atom, but it is hampered by dynamic heating conditions, as well as by the incomplete usage of the oxygen content in the system [4]. The present investigations are an attempt to enhance the usage of oxygen in the solid phase, and in this way to obtain greater quantities of ferrites.

There are similarities and differences in the processes of ferrite formation at 573 K and 1073 K.

It is common for these temperature conditions that the process starts with reaction (3). It can not be defined precisely whether BaO or BaO_2 participates in ferrite formation in the further interactions. Most probably, reaction (3) is the beginning of the process, and afterwards BaO_2 is the basic reagent, mainly as oxygen carrier. At 573 K, interactions between BaO_2 and FeOHSO_4 lead to the formation of

BaFeO₃, BaFe₂O₄ and BaSO₄, while there is no excess of BaO and/or BaO₂ in the system. The reactions proceed intensively, which is the cause of the rapid restructuring and initial growth of the new phases. X-ray and electron microscopy data prove this. Some peculiarities were found in the BaFeO₃ spectrum at 573 K. In mixtures with excess FeSO₄ ($n=4$ and 2), the BaFeO₃ spectrum is a single line, while in mixtures with $n=1$ the spectrum is a result of several overlapping lines, which form a split spectrum with a common isomeric shift of $\delta_{is}=0.45$ mm s⁻¹ and a common quadruple splitting of 0.23 mm s⁻¹ (Fig. 3). The BaFeO₃ obtained has a non-stoichiometric content of oxygen in its molecule and it is correct to use the general formula BaFeO_{*x*}, where $x=2.5-3.0$. This unstable structure makes it possible for BaFeO_{*x*} to participate in restructuring reactions, in which BaFe₂O₄ is obtained. However, it is quite possible that BaFe₂O₄ is a result of direct synthesis from FeO-HSO₄ and BaO₂.

The presence of BaFeO₃ has not been registered at 1073 K; only BaFe₂O₄ and BaFe₁₂O₁₉ have been detected in the end-products of decomposition (Table 1, Figs 4 and 5). It is most probable that at high temperatures this ferrite is formed in small quantities or is completely transformed to other ferrites.

The fundamental difference in the reactions of ferrite formation at 573 K and at 1073 K is the formation of BaFe₁₂O₁₉ at the higher temperature. Due to the system's quick transition through lower temperatures, the ferrite formation most probably proceeds in a reaction between BaO₂ and FeSO₄. It is supposed that the direct formation of BaFe₁₂O₁₉ is possible from the initial reagents. As in the investigations under dynamic heating conditions [4], it must be pointed that, due to the complex spectrum of BaFe₁₂O₁₉, in these experiments it has been identified via strongest lines in its spectrum (Fig. 5).

Mass losses. The mass losses in the thermal decomposition of the system FeSO₄·H₂O-BaO₂ at $n=4-1$ and 573 K remain comparatively constant in the range 8.9-10.3% (Table 1), regardless of the molar ratio of the reagents. This is so because, in mixtures with an excess of FeSO₄·H₂O ($n=4$ and 2), the mass losses are caused mainly by the dehydration of FeSO₄·H₂O to FeSO₄ and the partial oxidation to FeOHSO₄, while at $n=1$ they are the sum of dehydration, metathesis and ferrite formation. A comparison of the distribution of the iron in the decomposition end-products obtained at 573 K with those obtained under dynamic heating conditions shows that the quantity of barium ferrites at 573 K is almost twice as high. This could be evidence that the present investigations have created conditions for pushing the system equilibrium towards ferrite formation, while lesser quantities of barium are combined in BaSO₄.

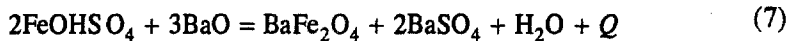
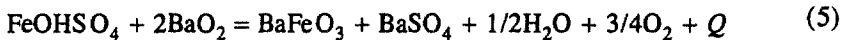
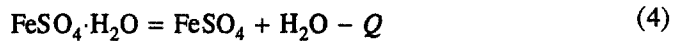
The mass losses at 1073 K are determined mainly by the desulphurization of FeSO₄, and to a lesser extent by dehydration of FeSO₄·H₂O to FeSO₄ and the formation of barium ferrites. Naturally, with increase of the BaO₂ content in the initial mixture, the overall mass losses decrease, as the quantities of ferrites and BaSO₄ increase in the decomposition end-products.

The established identical values for the distribution of iron in the products obtained at 1073 K and those obtained under dynamic heating conditions show that in the high-temperature range the mechanism of the process is not influenced considerably by the experimental conditions.

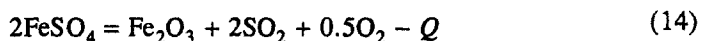
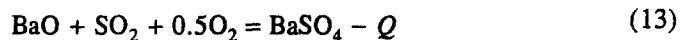
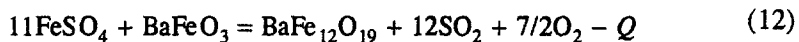
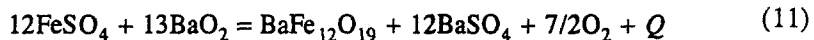
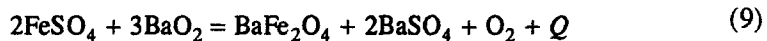
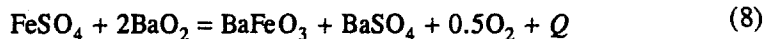
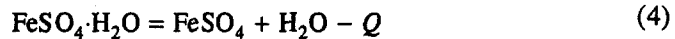
The most probable mechanism of the process of thermal decomposition at 573 and 1073 K.

The results of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O} - \text{BaO}_2$ in molar ratios of $n=4-1$, in closed crucibles and under isothermal heating conditions, indicate the following most probable mechanism:

$$T = 573 \text{ K}$$



$$T = 1073 \text{ K}$$



Inferences

There basic similarities and differences between the mechanisms of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O} - \text{BaO}_2$ mixtures in molar ratios of $n=4-1$, depending on the heating conditions.

The new experimental data confirm the possibility of the formation of barium ferrites (BaFeO_3 , BaFe_2O_4 and $\text{BaFe}_{12}\text{O}_{19}$) in the interactions in the low and high-temperature ranges, regardless of the heating conditions. The reactions are exothermic and proceed intensively, as proved by the small-scale crystalline phases and the non-stoichiometric compounds, i.e. BaFeO_3 , especially in mixtures with $n=1$.

The influence of the partial pressures of the gaseous components (water vapour, oxygen, and sulphur oxides) has similarly been confirmed. Changes of their values shift the equilibrium in the system. For $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, the change of $P_{\text{H}_2\text{O}}/P_{\text{O}_2}$, combined with the temperature conditions, leads to the formation of FeOHSO_4 and does not create conditions for the formation of $\text{Fe}_2\text{O}(\text{SO}_4)_2$, which shows that substantially influences the phase content of the ferrites obtained. Relative to the experiments under dynamic heating conditions, in the present investigations an almost doubled content was involved, in connection with barium ferrites in the low-temperature range. However, in the high-temperature range, as in previous investigations, the influence of P_{O_2} is very strong and leads invariably to the formation of BaSO_4 among the solid products of decomposition. This is most probably the cause of the roughly equal quantities of barium ferrites in the two types of experiments.

Conclusions

The experiments in the low-temperature range, where there is no desulphurization of FeSO_4 , and greater quantities of barium ferrites, are a premise to new investigations in different types of gaseous medium, i.e. vacuum or inert medium.

The proposed mechanism of thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O} - \text{BaO}_2$ mixtures with different molar ratios includes reactions where oxygen is released. To confirm this, it is necessary to carry out investigations on the same system through the ems method, which will be the object of future experiments.

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