

INVESTIGATION ON THERMAL DECOMPOSITION OF FeS₂ AND BaO₂ MIXTURES Part II

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Abstract

The thermal decomposition of FeS₂ and BaO₂ mixtures (mol ratio from 2 to 8) was studied in oxygen containing gas medium using dynamic heating rate. The solid decomposition products have been investigated with X-ray power diffraction and Mössbauer spectrometer. The thermal process has two main stages. In the presence of BaO₂ the mixtures have a lower initial temperature of iron sulfide burning. The same time by the increasing of BaO₂ content in the mixtures the diffusion difficulties are withdrawn in higher temperature ranges. It is proved that as intermediates BaSO₄, nonstoichiometric sulfide, barium ferrites and Fe₃O₄ are formed. The content of many solid phases in the final product is in relationship with the initial ratio of BaO₂ and FeS₂.

Keywords: barium peroxide, chemical transformations, mixtures, phase structures, pyrite, thermal decomposition

Introduction

By decreasing the initial temperature of burning we can intensify the process of FeS₂ oxidation [1]. The burning of FeS₂ and its mixtures with FeSO₄ is a subject of various investigations [2-4]. There are no literature data about pyrite oxidation in the presence of BaO₂.

The aim of the present work is to investigate the thermochemical decomposition of FeS₂ and BaO₂ mixtures in molar ratios $n=2-8$ in air medium.

Methods and techniques of investigation

The investigation was carried out under the conditions described in Part I for the same type of pyrite. Chemically pure BaO₂ 'REACHIM' - Russia was used, the main substance content in it being 95.07%. The Mössbauer analysis were carried out using a standard Mössbauer spectrometer operating under constant acceleration of a radioactive source (⁵⁷Co in Pd). The calibration of the rate scale was given in relation to α -Fe.

Results and discussion

The introduction of BaO₂ changes the mechanism of thermal decomposition of pyrite and the temperature ranges of transformation. This is quite well expressed in relation to the mass losses. With increasing BaO₂ content in the initial mixtures the final mass losses decrease, their amounts for pure FeS₂ being 25.8%; for $n=8$ —20.6% and for $n=4$ —16.4%. It is evident that these changes are connected with the interactions, taking place during two stages (Figs 1 and 2).

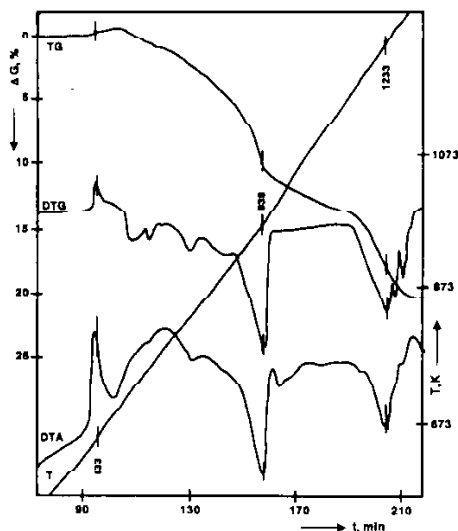


Fig. 1 Simultaneous TG, DTG, DTA curve of FeS₂ and BaO₂ mixture, $n=8$, $V=5$ K min⁻¹, air medium $G_s=1000$ mg

The first stage is realized in the 603–953 K temperature range and there are several simultaneous reactions typical for it. The initial increase of the sample mass, particularly well expressed for $n=4$ (Fig. 2), is accompanied by an intensive exothermic effect at $T=603$ –673 K. It is most probable that within this temperature range the structure of BaO₂ is destabilized under the influence of FeS₂. The released atomic oxygen attacks the molecule of FeS₂ and is a prerequisite for the beginning of its decomposition. As compared to pure pyrite [1] where this process starts at $T=683$ K, the initial temperature decreases by 80 K in the BaO₂ containing mixtures. The chemically active oxygen atom most probably attacks the weak van der Waals bondings in the structure of polysulphide, contributing to their destruction when elementary sulfur is released. It is oxidized to SO₃ and SO₂, which form BaSO₄ with parts of BaO₂ and BaO (Table 1).

Only in the mixtures containing greater amounts of BaO₂ ($n=2$), the Fe–S bondings are distracted when the partial pressure of active oxygen increases. These changes lead to an increase in the reactivity of the system, when as a result an analo-

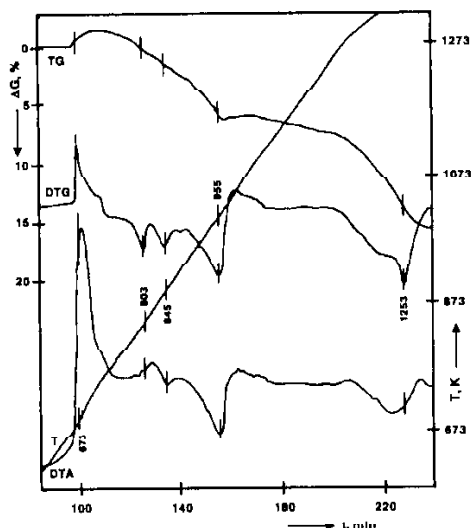


Fig. 2 Simultaneous TG, DTG, DTA curve of FeS₂ and BaO₂ mixture; $n=4$, $V=5$ K min⁻¹, air medium $G_s=1000$ mg

gous reaction as in the FeSO₄·H₂O–BaO₂ system [5, 6] takes place. In contrast to the FeSO₄·H₂O–BaO₂ system, in the FeS₂–BaO₂ one the exchange reaction takes place at a slightly higher temperature 633 K, but is accompanied by a distinctively more intensive exothermic effect. This is most indicative for the mixture with $n=2$ where the interaction takes place explosively, accompanied by an aerosol spraying out of about 50% of the mass of the sample. The mechanism of the process within the 603–713 K temperature range is clarified by the analysis of the TG curve, the Mössbauer spectroscopy and X-ray analysis of the intermediate products of decomposition. The spectrum of the product obtained by the treatment of a mixture with $n=4$ up to $T=693$ K (Fig. 3a) represents a doublet with slightly broadened lines, which proves the presence of FeS₂ in the sample. At single places on the background of the spectrum a certain broadening is recorded which is within the limits of the statistical deviation of impulses. Most probably these are the weakly expressed lines of the strongly narrowed sextets of pyrrhotine. We can say that the content in this phase is 1.0–1.5%. The broadening of the lines of FeS₂ provides evidence for the presence of about 3% of BaFeO₃.

While in the mixtures with $n=8$ and $n=4$, the content of the new phases is very low, their quantitative and qualitative composition in the obtained solid product after decomposition up to $T=683$ K is substantially changed when $n=2$ (Table 1 and Fig. 3b).

The spectrum shown in Fig. 3b consists of several overlapping sextets, a doublet and an inserted single line. The doublet is with $\delta_{is}=0.35$ mm s⁻¹ and $E_Q=0.63$ mm s⁻¹. It determines the presence of a phase in a paramagnetic state and refers to the not re-

Table 1 Data for the solid products from the decomposition of FeS₂ and BaO₂ mixtures in air medium

No.	T/ K	n	$\delta_{is}/$ min s ⁻¹	E_Q mm s ⁻¹	H_{eff} kOe	Fe/ %	Identified phases by					
							Mössbauer spectroscopy	X-ray analysis				
1.	693	4	0.37	0.65	-	97	FeS ₂	FeS ₂ , FeS, BaO ₂				
						3	BaFeO ₃		BaSO ₄			
2.	693	2	0.35	0.63	478	20	FeS ₂	BaSO ₄ , Fe ₂ O ₃				
			0.18	0.32		13	BaFe ₂ O ₄					
			0.40	0.42		42	α -Fe ₂ O ₃					
			-0.15	-		15	BaFeO ₃					
3.	1023	8	0.34	0.65	-	3	FeS ₂	FeS ₂ , FeS, Fe ₂ O ₃				
			0.73	0.00		23	A=Fe _{1-x} S+FeS x=0.1; 0.83		BaFeO ₃ , SiO ₂			
			0.73	0.00		260	14	B=Fe _{1-x} S+FeS x=0.1; 0.83	BaS, BaSO ₄			
			0.76	0.00		223	12	C=Fe _{1-x} S+FeS x=0.1; 0.83				
			0.30	0.10		-	3	BaFeO ₃				
			0.18	0.32		478	4	BaFe ₂ O ₄				
			4.	1211		4	0.35	0.43	519	38	α -Fe ₂ O ₃	FeS, Fe ₂ O ₃ BaSO ₄
							0.18	0.32		478	8	
-0.10	-	-			5		BaFeO ₃					
0.41	0.42	519			55		α -Fe ₂ O ₃					
					27		Fe _{1-x} S+FeS					
5.	1273	8	0.20	0.33	479	20	BaFe ₂ O ₄	Fe ₂ O ₃				
			0.40	0.42		517	73		α -Fe ₂ O ₃	BaSO ₄		
							7	BaFe ₁₂ O ₁₉	Fe ₂ O ₃ BaSO ₄ BaFeO ₃			
							60	α -Fe ₂ O ₃				
				20	BaFe ₂ O ₄							
				6	BaFeO ₃							
	1273	4	0.40	0.42	518	60	α -Fe ₂ O ₃	Fe ₂ O ₃				
			0.20	0.32		480	20		BaFe ₂ O ₄	BaSO ₄		
		-0.10	-	-	6	BaFeO ₃	BaFeO ₃					
					6	BaFe ₁₂ O ₁₉						
					8	Fe _{1-x} S+FeS						

acted in the exchange reaction FeS₂. The single line has an isomeric shift close to zero. Such a superposition is characteristic for compounds with perovskite structure of the BaFeO₃ type [7]. In the combination of different sextets, the most pronounced one is the α -Fe₂O₃ sextet. The next intensive sextet refers to a compound of spinel type as BaFe₂O₄. The other lines, which are more weakly expressed and in the greater part overlap with the lines of the two main phases – α -Fe₂O₃ and BaFe₂O₄, can be referred to the spectrum of BaFe₁₂O₁₉. This ferrite has a complex structure and its spectrum is a combination of 5 other subsextets. Its presence in the sample is proved by the presence of the strongest line 12k in its spectrum [8, 9]. Because of the small amount of BaFe₁₂O₁₉ in the sample, only the most external lines of its spectrum are marked in Fig. 3b.

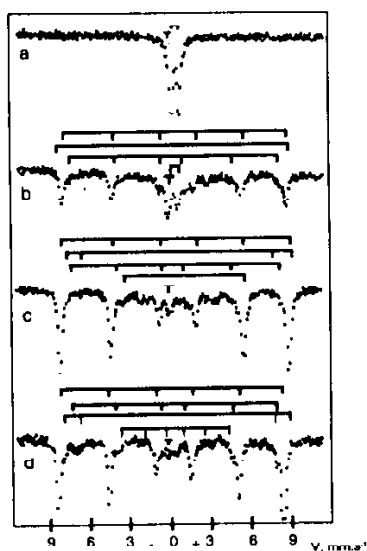
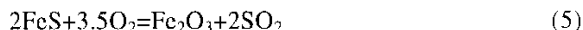
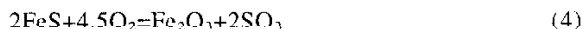
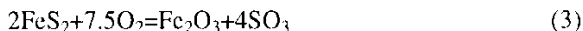


Fig. 3 Mössbauer spectra of solid products from thermochemical decomposition of pyrite and BaO₂ in air medium, $V=5 \text{ K min}^{-1}$; a) $n=4$, $T=693 \text{ K}$; b) $n=2$, $T=693 \text{ K}$; c) $n=4$, $T=1211 \text{ K}$; d) $n=4$, $T=1273 \text{ K}$

The analysis of the obtained results proves that within the 603–713 K temperature range the interactions take place with the formation of BaSO₄, pyrrhotines and small amounts of barium ferrites.

With the increase of the temperature from 713 to 939 K a dissociation and partial oxidation of pyrite takes place. The following reactions are characteristic for this process:





Depending on the BaO₂ content in the initial mixture the recorded mass losses change substantially. For example, the mass losses for pure FeS₂ [1] in the range of up to $T=961$ K are 19.2%; for $n=8$ up to $T=943$ K are 11.4% and for $n=4$ up to $T=955$ K are 7.2%. It is evident that the decrease of the mass losses with the increase of the BaO₂ amount in the initial mixtures results mainly from the BaSO₄ formation. The content of pyrrhotine in the intermediate products of decomposition is considerably changed depending on the molar ratio. Thus in pure FeS₂ [1] about 66% of the iron in the sample treated to $T=993$ K is present in the form of pyrrhotines, while in the case of $n=8$ and $T=1023$ K about 50% are registered. Again, as when decomposing pure pyrite, it can be determined by means of Mössbauer spectrometer data that the received mixture of nonstoichiometric pyrrhotines can be presented by the general formula Fe_{1-x}S+FeS, where $x=0.10-0.83$ (Table 1, Fig. 4a). The amount of iron in the form of α -Fe₂O₃ and FeS₂ is almost the same both for pure pyrite up to $T=993$ K and for a mixture with $n=8$ up to $T=1023$ K. Moreover, it is established that about 3% of the iron content in the solid product after decomposition of the sample with $n=8$ up to $T=1023$ K, is in the form of BaFeO₃ and about 7% – in the form of BaFe₂O₄.

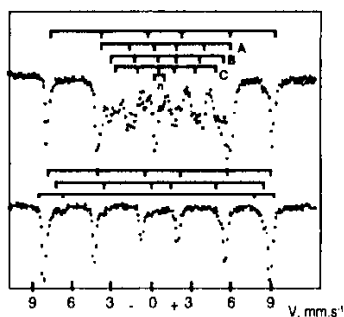


Fig. 4 Mössbauer spectra of solid products from thermochemical decomposition of pyrite and BaO₂ ($n=8$) in air medium, $V=5$ K min⁻¹; a) $T=1023$ K; b) $T=1273$ K

Within the 939–1183 K temperature range the changes in the course of the TG curves are insignificant. The recorded mass losses of 2.8% for $n=8$ (Fig. 1) and 1.4% – for $n=4$ (Fig. 2), are explained by the slow oxidation of the obtained pyrrhotine in the system to hematite. This is confirmed by the Mössbauer spectrometer analysis of the solid product after decomposing the mixture with $n=4$ up to $T=1211$ K (Fig. 3c). Its spectrum represents a combination of a multitude of sextets, the α -Fe₂O₃ one be-

ing of highest intensity. The spectra of the Fe_{1-x}S+FeS and BaFe₁₂O₁₉ mixtures are marked only by their strongest lines because of their complex structures and small amounts. Small quantities of BaFe₂O₄ – up to 8%, and BaFeO₃ – up to 5%, are found in the solid residue after the decomposition.

Within the 1183–1263 K temperature range a new step in the TG curve is distinctly observed (Figs 1, 2) which is not present when decomposing pure pyrite [1]. The recorded mass losses for $n=8$ amount to 6.4% (Fig. 1) and to 7.8% – for $n=4$ (Fig. 2). The analysis of the thermogravimetric dependencies, as well as of the Mössbauer spectrometer and X-ray data provide the ground to conclude that within the given temperature range oxidation of nonstoichiometric pyrrhotines to α -Fe₂O₃ takes place and the amounts of barium ferrites in the final products after the decomposition increase. The process is also accompanied by the formation of eutectic zones in the sample. The solid product after the decomposition of the mixture with $n=8$ (Table 1, Fig. 4b) contains about 73% of α -Fe₂O₃. The BaFe₂O₄ amount increases too. About 7% of the iron in the solid product after decomposition to $T=1023$ K (Fig. 4a) is in the form of BaFe₂O₄, while the amount of BaFe₂O₄ in the sample subjected to decomposition up to $T=1273$ K (Fig. 4b) is about 20%. Certain amounts of nonstoichiometric iron sulfides are recorded in the final product of the thermal decomposition up to $T=1273$ K (Fig. 3d) when the contents of BaO₂ in the initial sample ($n=4$) is higher. They are presented in Fig. 3d by weakly expressed and strongly narrowed sextets. The main phase is also α -Fe₂O₃ but about 32% of the iron is in the form of barium ferrites – BaFeO₃, BaFe₂O₄ and BaFe₁₂O₁₉.

The results obtained from derivatographic analysis, Mössbauer spectrometer analysis and X-ray phase analysis prove that the second stage of the thermal decomposition of FeS₂ and BaO₂ mixtures is shifted in the higher temperature range because of diffusion difficulties. The recorded mass losses are mainly connected with the oxidation of the obtained nonstoichiometric sulfides and to FeS₂ not decomposed to α -Fe₂O₃, as well as to the reformation of barium ferrites.

Conclusions

Thermal decomposition of FeS₂ and BaO₂ mixtures in air medium is carried out mainly within two temperature ranges, the initial temperature of lighting of pyrite being decreased by the presence of BaO₂. The effect of diffusion on the rate of decomposition increases with the rise of BaO₂ content in the initial mixtures. The Mössbauer spectrometer analysis and the X-ray phase analysis prove that the final products of decomposition contain Fe₂O₃, BaSO₄ and certain amounts of barium ferrites. The relative part of the ferrites (BaFeO₃, BaFe₂O₄ and BaFe₁₂O₁₉) in the solid products are a function of the molar ratio between FeS₂ and BaO₂. It is obvious that in the practice negligible quantities of BaO₂ could be recommended in order to intensify the process of pyrite decomposition.

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