

INVESTIGATION ON THERMAL DECOMPOSITION OF PYRITE

Part I

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Abstract

Thermochemical decomposition of pyrite in air-gas medium has been studied by means of MOM-Q 1500D Derivatograph. The derivatograms have been obtained at a heating rate of 5 K min⁻¹ and air flowrate of 25 l h⁻¹ to final temperatures of 833, 933 and 1273 K, chosen on the basis of the stepwise oxidation of pyrite. The solid product is analyzed using X-ray powder diffraction and Mössbauer spectrometer techniques. The formation of nonstoichiometric sulfides (pyrrhotines) as intermediates has been confirmed. The second stage of decomposition is the oxidation of these pyrrhotines to hematite. The recorded weight losses are lower than the theoretically possible because of the formed nonstoichiometric iron sulfides. The complicated structure of the intermediate products has been confirmed by means of other techniques.

Keywords: chemical transformations, phase structures, pyrite, thermal decomposition, thermal stability

Introduction

The investigations on solid phase oxidation of metal sulfides are connected with the problems of their industrial processing [1]. The various contradictions on the chemistry of the process of burning and dissociation of pyrite are explained by its complex structure, its origin, the presence of admixtures, gas medium and others [2-4]. The clarifying of the regularities and the mechanism of oxidation of FeS₂ is of great importance when choosing an optimum regime for its processing.

The aim of the present work is to investigate the thermochemical decomposition of pyrite in air-gas medium.

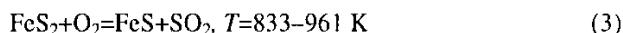
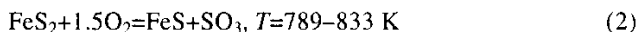
Methods and techniques of investigation

This investigation was carried out using a MOM-Q1500D derivatograph within the 293-1273 K temperature range at a heating rate of 5 K min⁻¹. The sample mass was 1000 mg and the air flowrate ~ 25 l h⁻¹. Zirconium crucibles with an inner diameter of 8 mm and a height of 20 mm were used. The pyrite composition (% wt.)

was as follows: 41.87 – S; 37.63 – Fe; 10.58 – SiO₂. The Mössbauer analyses were carried out using a standard Mössbauer spectrometer operating under constant acceleration of the radioactive source (⁵⁷Co in Pd). The calibration of the rate scale is given in relation to α-Fe.

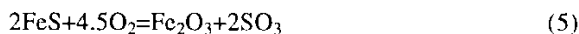
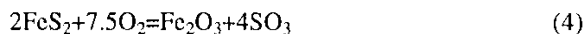
Results and discussion

The results of the thermal analyses of pure FeS₂ are presented in Fig. 1. Two major stages can be reported from the TG-, DGT- and DTA-curves of the process of thermal decomposition of pyrite. The first stage of its decomposition proceeds within the 683–961 K temperature range. The recorded weight losses amount to 19.7%. As known, pyrite is a typical representative of polysulphide. The leaning towards the formation of chain structures connected by weak Van der Waals bondings is their typical peculiarity. Thus the crystal obtains its layer structure. Initial destruction of these weak bondings, accompanied by liberation of elementary sulfur and partial oxidation of pyrrhotine and sulfur oxides begins most likely with the increase of temperature:



The burning of elementary sulfur and the formation of sulfur oxides affect the kinetics of pyrite decomposition, leading to the step-by-step character of the TG-dependence. At the same time the possibility of nonstoichiometric formation of sulfides of the Fe_{1-x}S type has to be taken into account. The intermediate products of pyrite decomposition in air medium up to $T = 833 \text{ K}$ (Table 1 and Fig. 2b) and $T = 993 \text{ K}$ (Table 1 and Fig. 2c) have been studied using X-ray analysis and Mössbauer spectroscopy.

The spectrum presented in Fig. 2b exhibits a doublet and two slightly manifested sextets. The main phase, which is in paramagnetic condition, is identified by its characteristics ($\delta_{is} = 0.35 \text{ mm s}^{-1}$ and $E_Q = 0.62 \text{ mm s}^{-1}$) as FeS₂. The two overlapping sextets could be referred to the γ- and α-Fe₂O₃ mixture. The presence of a mixture of low temperature and high temperature Fe₂O₃ modification is a proof that with the increase of temperature the oxidation of FeS₂ and FeS according to 4 and 5 proceeds at a higher rate than the dissociation and oxidation according to reactions 1–3:



It is evident that the transportation of oxygen atoms inside the sample is of great importance in the mechanism of reactions 4 and 5 – because of the higher layer of

FeS_2 , Fe_2O_3 originates mainly on the surface of the sample, where diffusion difficulties are more weak.

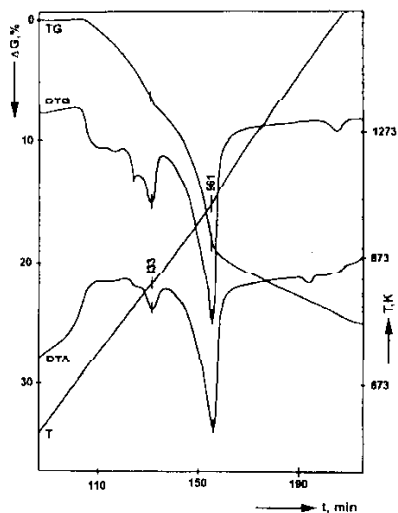


Fig. 1 Simultaneous TG, DTG, DTA curves of pyrite in air medium; $V=K \text{ min}^{-1}$; $G=1000 \text{ mg}$

Table 1 Solid substance after decomposition of FeS_2 in air

No.	T/ K	$\delta_{is}/$ mm s^{-1}	$E_G/$ mm s^{-1}	$H_{crit}/$ kOe	Fe/ %	Identified phases by:	
						Mössbauer spectroscopy	X-ray analysis
1	298	0.35	0.63	—	100	FeS_2	
2	833	0.35	0.62	—	87	FeS_2	FeS_2 , FeS
		0.40	0.42	518	13	γ - and α - Fe_2O_3	Fe_2O_3 , SiO_2
3	833	0.35	0.62	—	2–3	FeS_2	FeS_2 , FeS
		0.75	0.00	300	30	$A=\text{Fe}_{1-x}\text{S}$ $x=0.1-0.83$	Fe_2O_3 , SiO_2
		0.75	-0.20	257	20	$B=\text{Fe}_{1-x}\text{S}$ $x=0.1-0.83$	
		0.80	-0.20	223	16	$C=\text{Fe}_{1-x}\text{S}$ $x=0.1-0.83$	
4	1273	0.40	0.42	518	30	α - Fe_2O_3	
		0.40	0.43	518	100	α - Fe_2O_3	Fe_2O_3 , SiO_2

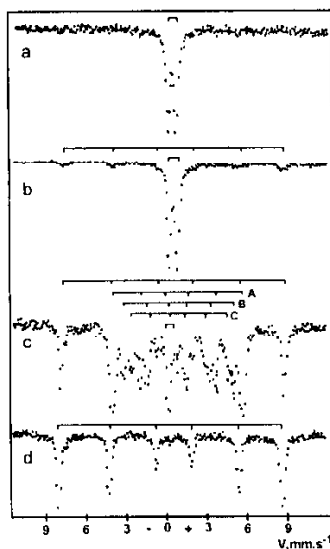
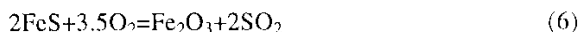


Fig. 2 Mössbauer spectra of solid products from the thermochemical decomposition of pyrite in air medium; a) initial FeS_2 ; b) up to 833 K; c) up to 993 K; d) up to 1273 K

With the increase of temperature and Fe_2O_3 quantity in the solid phase, the direct oxidation of pyrite to hematite is hampered and the governing reactions are 2 and 3. This is also supported by the results from the Mössbauer spectrometer analysis of the solid product after the thermal decomposition of FeS_2 up to 993 K (Fig. 2c). The sextet of $\alpha\text{-Fe}_2\text{O}_3$ is clearly expressed in the spectrum, but its inner lines are covered by other three strongly narrowed and mutually spreading one over another sextets. These three sextets identify the presence of pyrrhotine mixture in the sample. The analysis of the spectra and their characteristics, as well as of the available data in the literature [5], gives us ground to suppose that the obtained mixture of pyrrhotines is expressed more precisely by the general formula $\text{Fe}_{1-x}\text{S} + \text{FeS}$, where $x=0.10\text{--}0.83$, than by the formula $\text{FeS} + \text{Fe}_7\text{S}_8$.

Certain amounts of still non-decomposed FeS_2 are to be found in the solid product.

Under temperatures above 993 K oxidation of pyrrhotines to hematite is carried out as shown in Table 1 and Fig. 2d:



It is typical for the oxidation of pyrrhotine that under the created experimental conditions this process is not entirely completed at 1273 K. The recorded mass losses – 25.8% are lower than the theoretically possible ones which is an indication for diffusion retardation of the process due to the transportation of the gas components. The analyses of the final and intermediate solid products after decomposition of pure pyrite do not prove any formation of iron sulfates.

Conclusions

The experiments carried out on thermal decomposition of FeS_2 in air-gas medium corroborate the complex character of the reactions taking place. It is established that the partial pressure of the gas components and mostly of oxygen, exerts a considerable influence on the mechanism of the process and the temperature ranges of transformation. It has been proved that the oxidation of pyrite is connected with the formation of a mixture of non-stoichiometric iron sulfides of complex structure as intermediate products after the first step of pyrite decomposition.

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