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ON THE DECOMPOSITION OF $FeSO_4$ IN THE PRESENCE OF FeS_2 AND BaO_2

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$FeSO_4$ is a waste obtained in the production of TiO_2 and also in steel etching in block metallurgy. The thermochemical decomposition of different $FeSO_4$ - FeS_2 - BaO_2 mixtures was studied by means of a derivatograph, X-ray diffraction, Mössbauer spectroscopy, EMF and other methods in order to understand the chemical transformations, new solid phases and kinetic limitations in the temperature range 292 - 1292 K. It was shown that there is a multistep process in which $BaSO_4$, FeS, $BaFeO_3$ and $BaFe_2O_4$ can be formed as intermediates. Depending on the initial ratio of the components, the atmosphere and the temperature range, different phase compositions of the final solid product can be obtained. At the present stage of the investigations, the possibility of obtaining pure barium ferrite as a product is not confirmed.

Fe(II)sulphate is a factory waste obtained in the production of TiO_2 by the sulphate method and also in steel etching in black metallurgy [1, 2]. Thermochemical decomposition is one way to utilize it in the production of iron oxides and sulpur-containing gases. Irrespective of the organization of the process, the gas obtained should have an appropriate concentration for the preparation of sulphuric acid. The content of sulphur oxides in the output gases could be increased with pyrite in the mixture. The autothermality of the process of decomposition of dry sulphate in the combustion of flotation pyrite is attained at S_{sulphate}: S_{sulphide} 1:1.7-2 [2]. The use of barium peroxide in the system decreases the need for oxygen and leads to a lower expenditure of a gaseous reagent. It appears to be no literature reports on the processes that occur when the $FeSO_4$ - FeS_2 - BaO_2 system is heated.

The aim of the present work was to investigate the mechanism of thermochemical decomposition of a $FeSO_4$ - FeS_2 - BaO_2 mixture in a molar ratio of 4:8:1 in an oxidizing atmosphere at 1273 K.

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Experimental

Method

The investigations were carried out in a dynamic regime, at a heating rate of 5 deg/min, in the temperature range 293-1273 K, with Q-1500D derivatograph (MOM, Hungary). The sample weight was 1000 mg, and the rate of air delivery was 25 l/h. Zirconium melting-pots with an internal diameter of 8 mm and a height of 20 mm were used. The investigations were carried out with a pyrite concentrate containing 41.87 % S, 37.63 % Fe and 10.58 % SiO_2. The iron(II)sulphate and barium peroxide were chemically pure substances. BaO_2 was produced by "REACHIM", USSR; the content of the basic substance was 97.05 %. $FeSO_4.7H_2O$ was transformed into $FeSO_4.H_2O$ by preliminary drying at 353 K and 0.6 MPa. The contents of SO_4^{2-} and Fe^{2+} in the monohydrate were 58.93 % and 34.47 %. The intermediates and the final solid products obtained from the thermochemical decomposition were analysed by powder diffractometry and Mössbauer spectroscopy.

Results and discussion

Thermochemical decomposition of $FeSO_4$ and its mixtures with BaO_2

The thermochemical decomposition of pure $FeSO_4$ is characterized by several basic stages (Fig. 1). The initial weight loss of 2 % up to 433 K is due to moisture adsorbed from the air. The sample mass decreases by 6.7 % in the temperature range 478-595 K and coincides with loss of the molecule of water from the monohydrate. The height of the zirconium melting-pots and the comparatively large quantity of sample hamper the complete dehydration process and lead to weight losses smaller than the theoretical one. We assume that the process continues at higher temperatures and terminates with the beginning of thermochemical decomposition of dry $FeSO_4$. Some change was recorded in the TG run in the temperature interval 763-805 K. The atmospheric oxidation of Fe^{2+} to Fe^{3+} and the formation of $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$, etc. is possible in this temperature range [3]. By means of X-ray phase analysis, we have proved only the formation of $FeOHSO_4$ in the products of dehydration of $FeSO_4$ (Fig. 2). The change in the TG run supported the assumption of immediate dehydration and oxidation. It was difficult to explain the presence of metastable iron compounds due to the

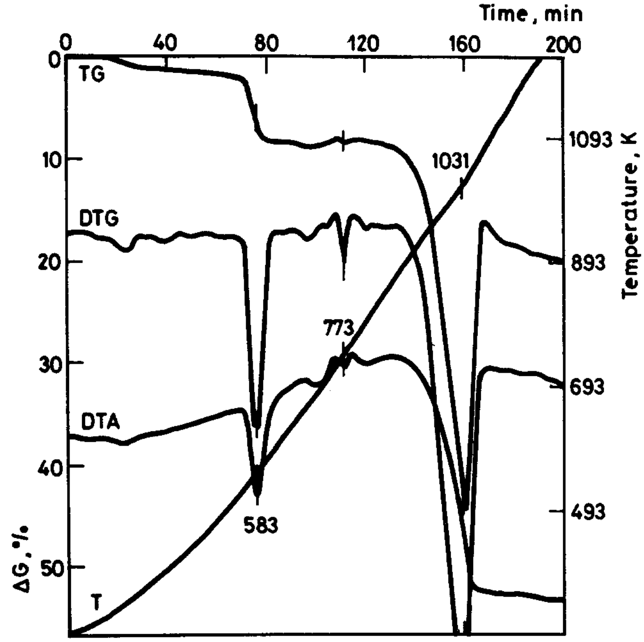

Fig. 1 TG, DTG and DTA curves of the thermal decomposition of $FeSO_4 \cdot H_2O$ at $T = 1273$ K

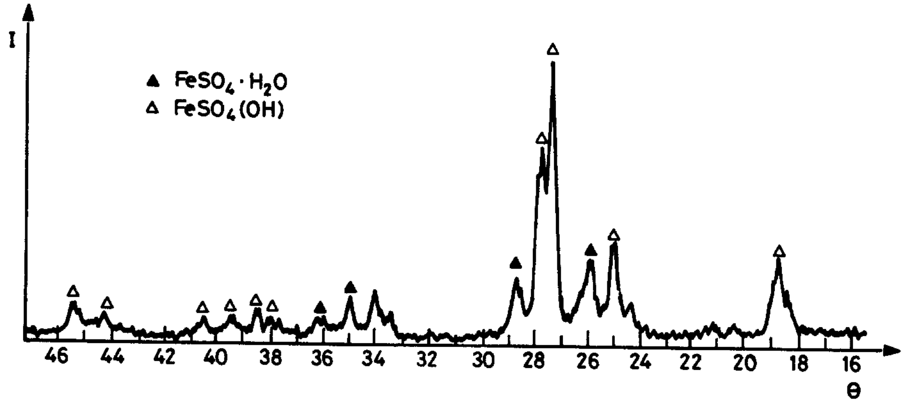

Fig. 2 X-ray of a product from the thermal decomposition of $FeSO_4 \cdot H_2O$ at 595 K

strong influence of temperature and the partial pressure of oxygen on the preparation. Due to the height of the sample and the difficulty of access of oxygen atoms to the interior of the sample, these compounds are probably formed in very small quantities and could not be detected by X-ray phase analysis. The process of desulphurization of $FeSO_4$ begins at 833 K and the DTA curve shows a deep endothermal effect.

The process terminates at 1083 K and Fe_2O_3 is obtained in the solid product. The TG sample weight loss of 45 % confirms the formation of hematite.

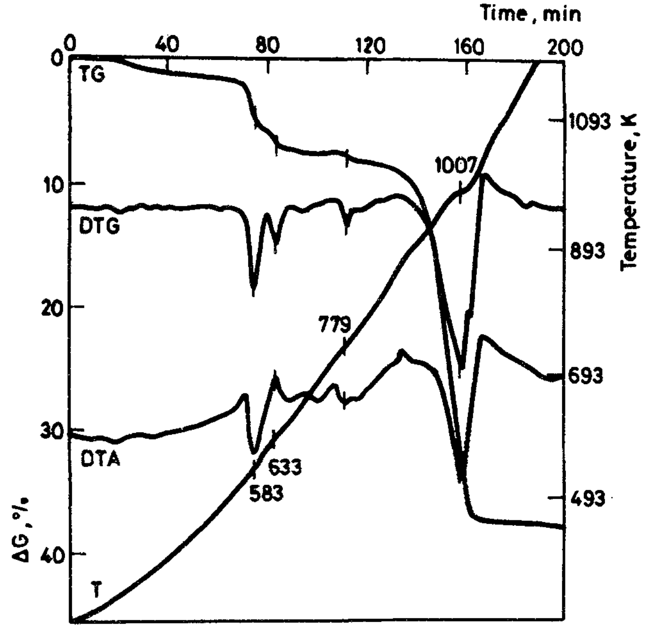

Fig. 3 TG, DTG and DTA curves of the thermal decomposition of a mixture of $FeSO_4$ and BaO_2 in molal ratio of 4:1 at $T = 1273$ K

The introduction of BaO_2 into the system changes the mechanism and the kinetics of the process significantly. Figure 3 presents a derivatogram of the thermochemical decomposition of a $FeSO_4$-BaO_2 mixture in a molar ratio of 4:1. Two consecutive processes were indicated by the TG dependence in the temperature interval 553-659 K. The first of these is connected with the loss of water from the $FeSO_4 \cdot H_2O$, as indicated by the weight loss of 4 % and the endo effect in the DTA curve. Evidently, the thermal dissociation of BaO_2 begins in the given temperature range. The atomic oxygen formed is very reactive and attacks the $FeSO_4$ in the system. This leads to an exchange reaction between the components at 613 K and the formation of

Fe_2O_3 and $BaSO_4$ accompanied by the evolution of heat. The process can be illustrated by the following equation:

$$FeSO_4 + BaO_2 \rightarrow BaSO_4 + 0.5\,Fe_2O_3 + 0.25\,O_2 \qquad (1)$$

A slight process of intermediate oxidation and decomposition in the temperature range 759-779 K, characteristic of the pure sulphate, was also observed. The main process of desulphurization of the excess of $FeSO_4$, takes place after the exchange reaction between $FeSO_4$ and BaO_2. It occurs in the temperature interval 883-1063 K and results in a weight loss of 28.3%. It can be seen that the introduction of BaO_2 and the formation of $BaSO_4$ leads to a shift in the initial temperature of decomposition of $FeSO_4$ to higher values and to a decrease in the total mass loss of 54.6% : 37.3% for pure $FeSO_4$; 45% for the mixture of $FeSO_4$ and BaO_2, as well as weight losses owing only to desulphurization of $FeSO_4$; 28.3% for pure $FeSO_4$ obtained from the thermochemical decomposition of the mixture. The presence of $BaSO_4$ and Fe_2O_3 (Fig. 4) in the final products of decomposition was established by means of X-ray phase analysis.

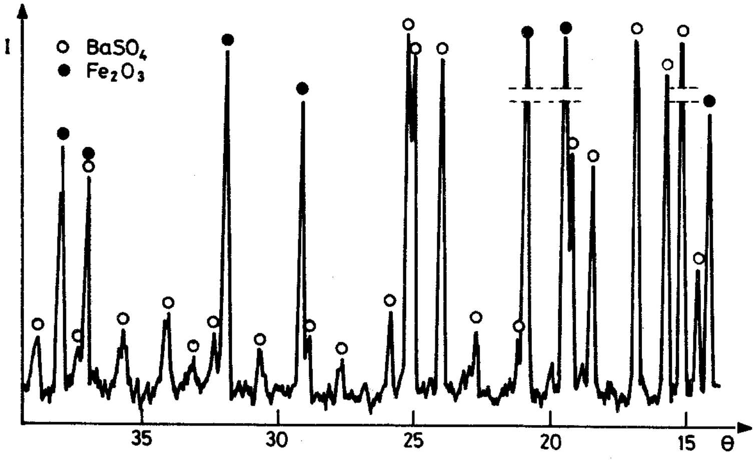

Fig. 4 X-ray of a product from the thermal decomposition of a mixture of $FeSO_4$ and BaO_2 in molal ratio of 4:1 at $T=1273$ K

Thermochemical decomposition of FeS_2 and its mixtures with BaO_2

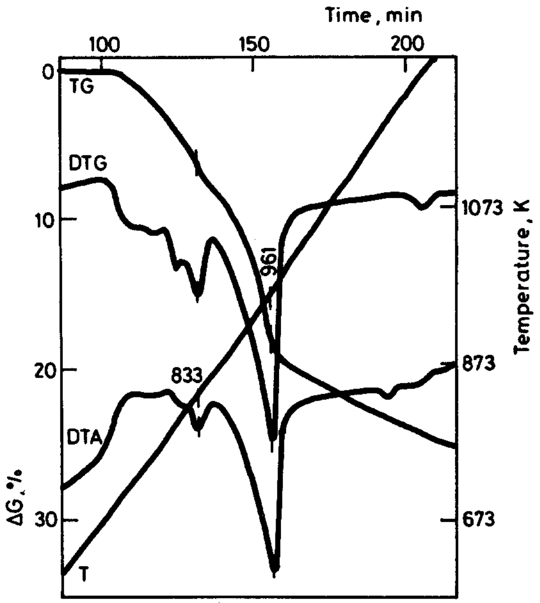

Fig. 5 TG, DTG and DTA curves of the thermal decomposition of FeS_2 at $T=1273$ K

The derivatogram of the thermochemical decomposition of FeS_2 is shown in Fig. 5. The literature data for the thermochemical decomposition of FeS_2 [4] are very contradictory as concerns the mechanism of oxidation and depend on the type of the investigated pyrite concentrate and the experimental conditions. Analysis of the TG, DTA and DTG dependences leads to some conclusions about the processes of dissociation and oxidation of FeS_2 under a dynamic heating regime. The first stage of decomposition of FeS_2 occurs in the temperature range 637-901 K. On the basis of the weight loss of 19.2 %, this stage is probably connected with the dissociation of FeS_2, as represented by the following equations:

$$FeS_2 \rightarrow FeS + S \qquad T=637\text{-}781\ \text{K} \qquad (2)$$

$$FeS_2 + 1.5\ O_2 \rightarrow FeS + SO_3 \qquad T=781\text{-}829\ \text{K} \qquad (3)$$

$$FeS_2 + O_2 \rightarrow FeS + SO_2 \qquad T=829\text{-}901\ \text{K} \qquad (4)$$

The combustion of elementary sulphur and the formation of sulphur oxides lead to alterations in the kinetics of decomposition of FeS_2, registered with a step character in the TG plot. The possible formation of nonstoichiometric sulphides of the type $Fe_{1-x}S$ should be mentioned. At above 961 K, the oxidizing process proceeds at constant rate and pyrotine is converted into hematite:

$$2\,FeS + 3.5\,O_2 \rightarrow Fe_2O_3 + 2\,SO_2 \qquad (5)$$

The characteristic feature of the process of thermochemical decomposition of pyrotine is its inability to take place completely at 1273 K. The experimental weight loss of 25.8 % is lower than the theoretical one, and shows the influence of the rate of transport of the gaseous reagents. Analysis of the intermediates and final products of the decomposition of pure FeS_2 does not prove the formation of iron sulphates.

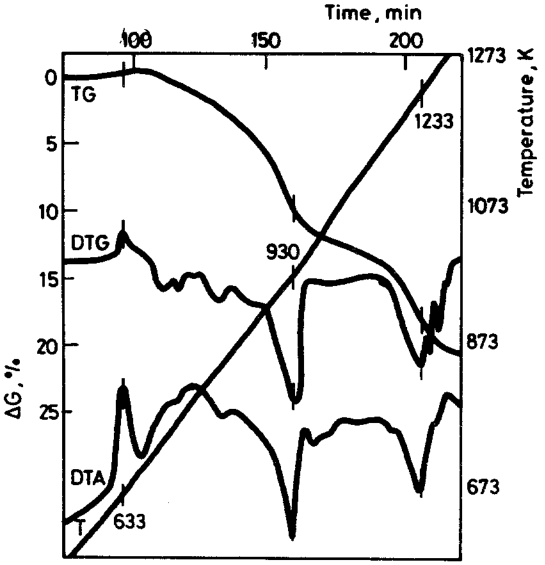

Fig. 6 TG, DTG and DTA curves of the thermal decomposition of a mixture of FeS_2 and BaO_2 in molal ratio of 8:1 at $T = 1273$ K

The introduction of BaO_2 into the system leads to changes in the mechanism and the temperature intervals of transformation. Figure 6 shows the derivatogram of the thermochemical decomposition of a mixture of FeS_2 and BaO_2 in the molar ratio 8:1. The process is a multistep one. The first stage occurs in the temperature range 609-759 K, and involves some possible parallel reactions. The increase of the temperature and the catalytic influence of FeS_2 destabilize the structure of BaO_2. The separating atomic oxygen attacks the FeS_2 molecule and predetermines the beginning of dissociation of elementary sulphur from its structure. The reactions that occur increase the reactivity of the components in the system and lead to the exchange reaction. This complicated mechanism of the process up to 759 K is confirmed by the slight increase in the sample mass at 681 K. The thermochemical decomposition of the double mixtures of $FeSO_4$ - BaO_2 and FeS_2 - BaO_2 indicates an exchange reaction at the higher temperature of 633 K. The exchange process is accompanied by a strong exothermal effect on DTA. This stage is well described by the following reaction:

$$0.75\ O_2 + FeS_2 + BaO_2 \rightarrow 0.5\ FeS + 0.5\ BaFeO_3 + 0.5\ BaSO_4 + S \quad (6)$$

Thermodynamic calculations confirm the possible formation of some barium ferrites, such as $BaFeO_3$ and $BaFe_2O_4$. The thermodynamic formation of $BaFe_2O_4$ is most probable. Under these conditions, however, the available oxygen in the system is not enough for the formation of $BaFe_2O_4$. The increase of the temperature from 759 to 939 K is accompanied by a continuous dissociation of FeS_2 according to reactions (2) - (4). The X-ray phase analysis data (Fig.7) show that the solid product obtained from the thermochemical decomposition of FeS_2 - BaO_2 in this temperature range contains FeS_2, FeS, $BaFeO_3$ and $BaSO_4$. The recorded weight loss of 11.4% also confirms the assumption of the existence of such a mechanism of the

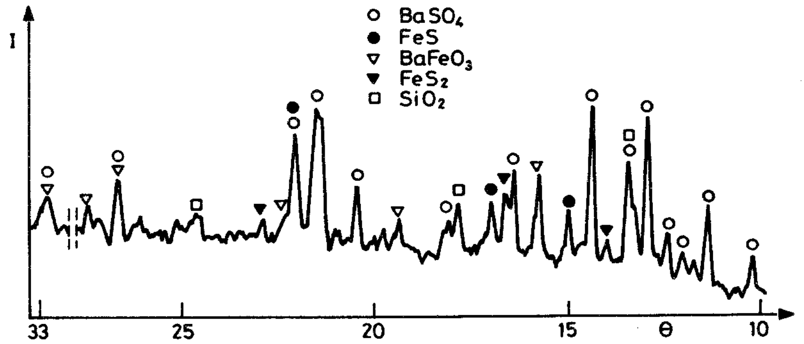

Fig. 7 X-ray of a product from the thermal decomposition of a mixture of FeS_2 and BaO_2 in molal ratio of 8:1 at T=983 K

process. The TG changes are negligible in the temperature range 939-1163 K. A weight loss of 2.8 % is registered, which is explained by the slow oxidation of pyrotine to hematite in the system.

The oxidation in the temperature range 1165-1263 K is more intensive and the rate of the process is higher. The mass loss is 6.4%. The total weight loss is lower than that from the thermochemical decomposition of pure FeS_2 due to the formation of $BaSO_4$ in the system. X-ray phase analysis and Mössbauer spectroscopy of the final product of the decomposition of FeS_2 - BaO_2 (Figs 8 and 9) indicate that $BaSO_4$, Fe_2O_3 and about 20% of $BaFe_2O_4$ were obtained. The Mössbauer spectrum of a sample after the thermal treatment of FeS_2 - BaO_2 in a molar ratio of 8:1 at 1263 K exhibits a combination of two sextets (Fig. 9). One of them is characteristic of the α-Fe_2O_3 spectrum, while the other one, with slight lines, is due to $BaFe_2O_4$. In order to explain the mechanism and the temperature intervals of the phase transitions of the barium ferrites, the solid products of the decomposition of FeS_2 - BaO_2 in a molar ratio of 8:2 at a temperature not higher than 1211 K or 1263 K were investigated by means of Mössbauer spectroscopy. The spectrum of the solid product obtained up to 1211 K (Fig. 10) reveals the spectrum of α-Fe_2O_3 and vague spectra of non-stoichiometric iron sulphides and barium ferrites: $BaFeO_3$ and $BaFe_2O_4$. Figure 10 shows the presence of iron sulphides with a narrow sextet, the intensity of which indicates that the quantity in the sample is about 8-10 %. Barium metaferrite has a perovskite structure. Compounds of this type give a Mössbauer spectrum consisting of

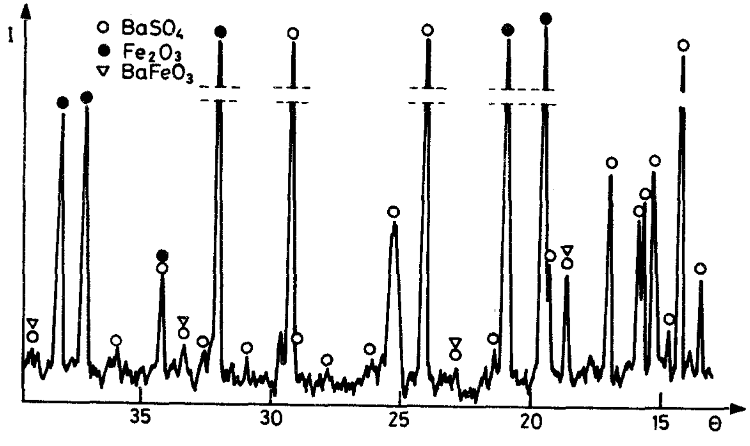

Fig. 8 X-ray of a product from the thermal decomposition of a mixture of FeS_2 and BaO_2 in molal ratio of 8:1 at $T = 1273$ K

a single line with an isomer shift near to zero. Nevertheless, some widening of the α-Fe_2O_3 lines is seen, which proves the presence of $BaFe_2O_4$. The main quantity of ferrite is in the form of $BaFeO_3$. The spectrum of the solid product from the decomposition of FeS_2 - BaO_2 in a molar ratio of 8:2 at 1263 K again reveals a combination of several sextets (Fig. 11). The lines of the α-Fe_2O_3 spectrum are well expressed. Comparison with the spectrum in Fig. 9 shows the presence of 15-20 % of $BaFe_2O_4$ and about 5 % of $BaFeO_3$ in the sample.

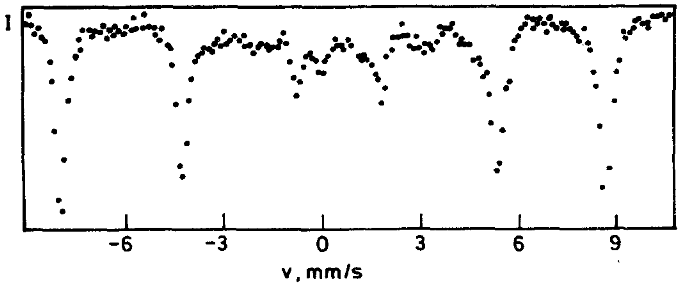

Fig. 9 Mössbauer spectrum of a product from the thermal decomposition of a mixture of FeS_2 and BaO_2 in molal ratio of 8:1 at $T = 1273$ K

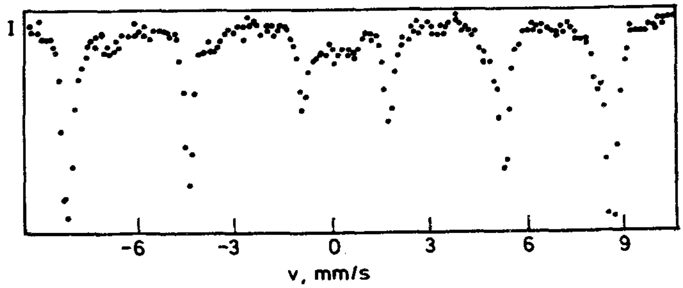

Fig. 10 Mössbauer spectrum of a product from the thermal decomposition of a mixture of FeS_2 and BaO_2 in molal ratio of 8:2 at $T = 1211$ K

The results of Mössbauer spectroscopy allow conclusions on the mechanism of the processes in the system FeS_2 - BaO_2 in the temperature ranges 939-1163 K and 1163-1263 K.

Besides the oxidation of pyrotine to hematite in the temperature range 939-1163 K, the transformation of $BaFeO_3$ to $BaFe_2O_4$ begins. The ratio $BaFeO_3$:$BaFe_2O_4$ is 4:1. Together with the intensive oxidation of iron sul-

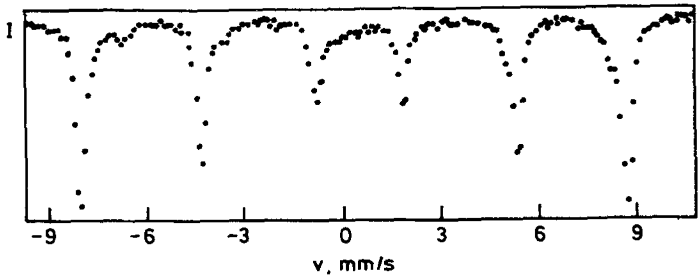

Fig. 11 Mössbauer spectrum of a product from the thermal decomposition of a mixture of FeS_2 and BaO_2 in molal ratio of 8:2 at $T = 1273$ K

phide, the phase transition of $BaFeO_3$ into $BaFe_2O_4$ increases. Both processes terminate at about 1253 K. The ratio of $BaFeO_3$ and $BaFe_2O_4$ in the solid phase is approximately 1:4.

Thermochemical decomposition of $FeSO_4$ in the presence of pyrite concentrate

Figure 12 shows a derivatogram of the thermochemical decomposition of a mixture of $FeSO_4$ and FeS_2 in a molar ratio of 4:8. In the temperature range 523-659 K, the system loses only crystal water from the monohydrate, with a weight loss of about 2.5 %. A significant weight loss of 23 %, which exceeds the theoretical possibility for complete dissociation of FeS_2 to pyrotine, is registered in the temperature range 683-803 K. The TG run is characteristic of a self-increasing process. Evidently, the intensive separation of elementary sulphur and sulphur oxides as a result of pyrotine formation and of the partial decomposition of $FeSO_4$ begins after 683 K:

$$0.5\,O_2 + 2\,FeSO_4 \xrightarrow{S,SO_3} Fe_2O_3 + 2\,SO_3 \qquad (7)$$

$$0.5\,O_2 + 3\,FeSO_4 \xrightarrow{S,SO_3} Fe_3O_4 + 3\,SO_3 \qquad (8)$$

The process of decomposition of $FeSO_4$ begins at 763 K, which is lower than the initial temperature (833 K) of dissociation of pure $FeSO_4$ (Fig. 1). Thus, the FeS_2 in the solid phase and the separated sulphur act as catalysts and decrease the temperature of decomposition of $FeSO_4$. Saffiullin [5] and Vassilev [2] obtained similar results. The accumulation of the products of reactions (2)-(4) and (7), and the presence of SO_2 and SO_3, lead to blockade of the thermochemical decomposition of $FeSO_4$. Increase of the temperature from 803 K to 853 K leads to dissociation of the residual undecomposed FeS_2 according to reactions (3) and (4). The weight loss of 4.5% corresponds to the dissociation of about 35 % of the FeS_2 concentrate in the sample. The remaining 65 % dissociates together with $FeSO_4$ in the previous stage. The processes of dissociation an oxidation of FeS_2 and pyrotine are accompanied by decomposition of the $FeSO_4$ excess. The process takes place in the temperature range 853-1011 K and coincides with the decomposition of pure $FeSO_4$ (Fig. 1). The registered 7.7 % weight loss shows that 40 % of the $FeSO_4$ decomposes; the remaining 60 % is decomposed in parallel with $FeSO_2$ oxidation. The last stage occurs in the temperature range 1011-1233 K. This is characterized by oxidation of the accumulated FeS to Fe_2O_3. This is proved by the X-ray diagram of the final product of decomposition of the mixture (Fig. 13).

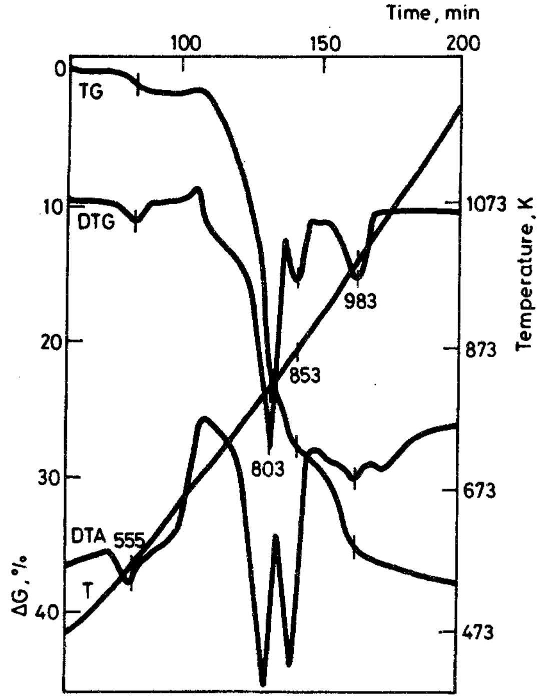

Fig. 12 TG, DTG and DTA curves of the thermal decomposition of a mixture of $FeSO_4$ and FeS_2 in molal ratio of 4:8 at $T = 1273$ K

The simultaneous decomposition of FeS_2 and $FeSO_4$ in a molar ratio of 4:8 shows the significant intensification of the process of oxidation and dissociation of FeS_2 and $FeSO_4$. The formation of $Fe_{1-x}S$ from pure FeS_2 occurs at 961 K (Fig. 5). The same process in mixtures with $FeSO_4$ takes place at a temperature not higher than 853 K. The destruction of the $FeSO_4$ structure in the presence of FeS_2 is a two-stage process which begins at the lower temperature of 763 K (Fig. 12).

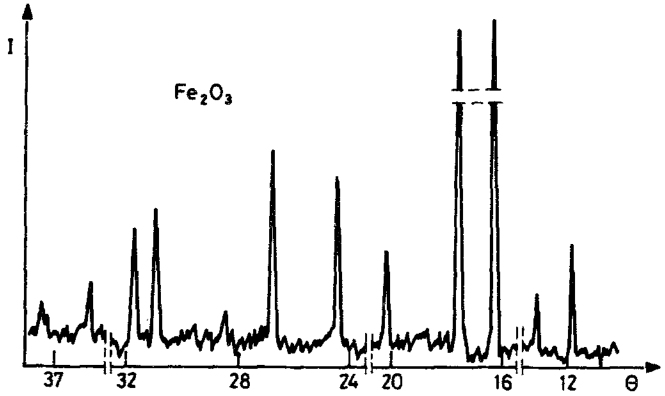

Fig. 13 X-ray of a product from the thermal decomposition of a mixture of $FeSO_4$ and FeS_2 in molal ratio of 4:8 at $T = 1273$ K

Thermochemical decomposition of the system $FeSO_4$ - FeS_2 - BaO_2

Figure 14 gives the derivatogram of the thermochemical decomposition of the system $FeSO_4$ - FeS_2 - BaO_2 in the molar ratio 4:8:1. The TG run is characterized by three consecutive stages corresponding to three endothermal effects. The largest mass loss of 17.4 % is that of the first stage, at 693-823 K. The second stage is from 823 K to 883 K, with an almost linear mass decrease of 3.5 %. The mass decreases by 6.1 % in the temperature interval 883-1007 K. The desulphurization of the undecomposed $FeSO_4$ to hematite is similar to that in the double system $FeSO_4$ - FeS_2. The TG run in the temperature range 693-983 K is very similar to the for the double system $FeSO_4$-FeS_2 which shows that the processes of desulphurization of FeS_2 and $FeSO_4$ determine the basic mechanism of the process. The mixture loses 1.9 % more mass at 1073-1243 K, but a well expressed endo effect is registered at 1223 K. The weight loss is most probably connected with the formation of thyoline. Analysis of the enthalpic-changes and weight losses suggests the following scheme for the chemical mechanism of the process:

$$FeSO_4 xH_2O \xrightarrow{533-593K} FeSO_4.yH_2O + (x\text{-}y)\ H_2O \tag{8}$$

$$BaO_2 \xrightarrow{593-653K} BaO + 0.5\ O_2 \tag{9}$$

$$2\ FeSO_4.yH_2O + BaO_2 \xrightarrow{633-693K} BaSO_4 + 2y\ H_2O + Fe_2O_3 + SO_3 \tag{10}$$

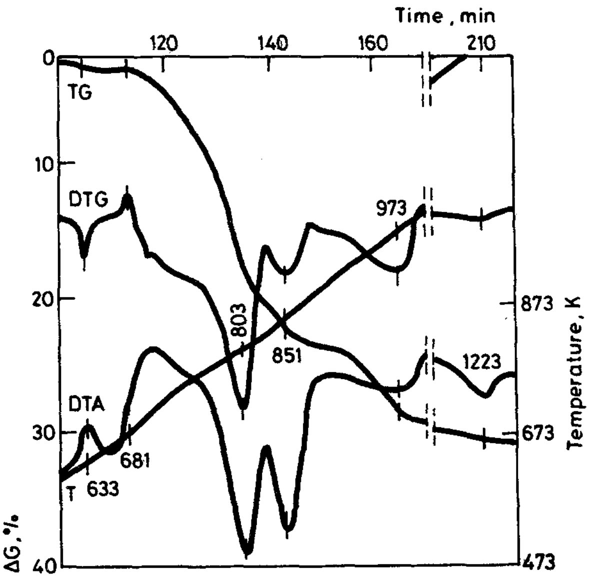

Fig. 14 TG, DTG and DTA curves of the thermal decomposition of a mixture of $FeSO_4$, FeS_2 and BaO_2 in molal ratio of 4:8:1 *at* T = 1273 K

$$FeSO_4.yH_2O + 0.5\ O_2 \xrightarrow{673-693K} FeOHSO_4 + (y/2)\ H_2O \tag{11}$$

$$FeS_2 \xrightarrow{693-823K} FeS + S \tag{2}$$

$$FeS_2 + 1.5\ O_2 \xrightarrow{823-873K} FeS + SO_3 \tag{3}$$

$$2\ FeSO_4 \xrightarrow{883-983K} Fe_2O_3 + 2\ SO_2 + 0.5\ O_2 \tag{12}$$

The separation of oxygen in the temperature range 593-693 K is proved by measurement of the oxygen partial pressure in the system by the EMF method with a CaO - ZrO_2 sensor.

At the same time, other barium ferrite products registered in different systems confirm that the chemical mechanism includes other interactions as well.

Table 1 The values of activation energy (*E*) for different steps decomposition of mixtures from $FeSO_4$-FeS_2-BaO_2 system

No	System	*T*, K	*E*, kJ/mol	*K*
I	$FeSO_4.xH_2O$			
1	$FeSO_4.xH_2O = FeSO_4.yH_2O + (x-y).H_2O$	545-645	71.4	0.990
2	$2FeSO_4 = Fe_2O_3 + 2SO_2 + 0.5O_2$	770-1090	136.9	0.997
II	FeS_2			
1	$FeS_2 = FeS + S$	683-853	96.6	0.996
2	$FeS_2 + 1.5O_2 = FeS + SO_3$	853-993	123.0	0.999
III	$FeSO_4 + BaO_2 = 4:1$			
1	$2FeSO_4 = Fe_2O_3 + 2SO_2 + 0.5O_2$	1050-1100	130.8	0.989
IV	$FeS_2 + BaO_2 = 8:1$			
1	$2.5FeS_2 + BaO_2 + 3O_2 = 0.5BaFeO_3 + + 0.5BaSO_4 + FeS_2 + FeS + 1.5SO_3$	609-973	49.6	0.822
2	$2FeS_2 + 3.5O_2 = Fe_2O_3 + 4SO_2$	1163-1263	155.3	0.996
V	$FeSO_4 + FeS_2 = 4:8$			
1	$FeSO_4 + FeS_2 + 3.75O_2 = 0.5Fe_2O_3 + FeS + + 2SO_3$	683-809	104.5	0.999
2	$FeS_2 + 1.5O_2 = FeS + SO_3$	809-853	118.34	0.991
3	$2FeSO_4 = Fe_2O_3 + 2SO_2 + 0.5O_2$	853-1011	125.3	0.998
VI	$FeSO_4 + FeS_2 + BaO_2 = 4:8:1$			
1	$2FeSO_4 + 2FeS_2 + BaO_2 + 1.25O_2 = FeS_2 + + FeSO_4 + FeS + BaSO_4 + 0.5Fe_2O_3 + SO_3$	633-823	96.9	0.995
2	$FeS_2 + 1.5O_2 = FeS + SO_3$	823-883	100.2	0.998
3	$2FeSO_4 = Fe_2O_3 + 2SO_2 + 0.5O_2$	883-1007	126.1	0.998

Table 1 gives the results of mathematical processing of the experimental data on the basis of the generalized equation of Reich [6] and the Arrhenius equation:

$$d\alpha/dt = A/B.e^{E/RT}(1-\alpha)^n \qquad (13)$$

where: α is the degree of transformation

T is the temperature (K)

B is the rate of heating (deg/min)

A is the preexponential factor
E is the activation energy (kJ/mol)
R is the universal gas constant (kJ/mol)
n is the order of reaction

The different activation energy values obtained illustrate the different rates of the dominating reactions in the given temperature ranges and demonstrate the possibly more effective reprocessing of waste $FeSO_4$.

Conclusion

Complex investigations on the decomposition of $FeSO_4$ in mixtures containing pyrite concentrate and barium peroxide show that, depending on the molar ratio of the components in the output mixtures and the final temperature of the thermochemical decomposition, the preparation of solid products with different compositions and properties is possible. The possibility of obtaining a final product of barium ferrite at the present stage of the investigations is not confirmed.

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Zusammenfassung — $FeSO_4$ ist ein Abfallprodukt aus der Herstellung von TiO_2 und aus dem Stahlätzen in der Blockmetallurgie. Mittels Derivatographie, Röntgendiffraktion, Mössbauerspektroskopie, EMF und anderen Methoden wurde die thermochemische Zersetzung verschiedener $FeSO_4$ - FeS_2 - BaO_2 - Gemische untersucht, um chemische Umformungen, neue Festphasen und kinetische Grenzen im Temperaturbereich 292-1292 K zu verstehen. Es wird die Existenz eines mehrstufigen Prozesses gezeigt, in dem $BaSO_4$, FeS, $BaFeO_3$ und $BaFe_2O_4$ als Zwischenprodukte geformt werden können. In Abhängigkeit von dem Ausgangsverhältnis der Komponenten, der Zusammensetzung der Atmosphäre und des Temperaturbereiches können für das feste Endprodukt verschiedene Phasenzusammensetzungen erhalten werden. Im gegenwärtigen Stadium der Untersuchungen konnte die Möglichkeit von reinem Bariumferrit als Produkt nicht bestätigt werden.