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# KINETICS AND MECHANISM OF THE NATURAL MINERAL MARMATITE OXIDATION PROCESS

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## Abstract

Results obtained by the comparative investigations of the natural mineral marmatite (Zn,Fe)S (Stari Trg, Yugoslavia) oxidation process are presented in this paper.

Determination of the oxidation process mechanism was done by thermal analysis methods: DTA-TG-DTG and DSC, while Mössbauer spectroscopy, X-ray and electronic microanalysis were used for phase composition determination of the products formed during the oxidation process. Kinetics of the process was defined for two temperature intervals 862–973 and 1023–1173 K, under isothermal conditions.

**Keywords:** kinetics, marmatite, oxidation process

## Introduction

Process of zinc sulfide oxidation, which was investigated by several authors [1–5], is of the great importance for the metallurgy of zinc. Beside the formation of ZnO, during the oxidation process in the system Zn–Fe–S–O, less dissolvable in the leaching process $ZnFe_2O_4$ is formed, which influences zinc losses. The presence of marmatite ($m$ZnS·$n$FeS or (Zn,Fe)S) in zinc concentrates, increases the possibility of $ZnFe_2O_4$ formation during the oxidation process [6], and zinc losses during the leaching process as well.

Results of the oxidation process investigations of pure natural mineral marmatite are presented in this paper, with the intention to determine the kinetics and mechanism of the process not full explained and described in literature.

## Experimental

Pure mineral marmatite (Stari Trg, Yugoslavia) was used for the experimental investigations. Chemical composition of the investigated sample was as follow-

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ing: 48.30% Zn, 19.25% Fe, 31.80% S and 0.65% rest, which correspond to the formula $(0.29Fe\cdot 0.71Zn)S$ or $0.29FeS\cdot 0.71ZnS$ for the investigated marmatite.

DTA-TG-DTG analysis were done on a Derivatograph 1500, MOM Budapest, DSC investigations on DSC-404 Netzsch, electronic microanalysis on microsond Joel Super 733; Mössbauer spectroscopy on Mettler spectrometer and X-ray analysis on Siemens apparatus with a Cu anticathode.

## Results and discussion

DTA-TG-DTG curves for the marmatite oxidation process, obtained at heating rate of 10°C min$^{-1}$ in an air atmosphere, are shown in Fig. 1, while DSC curves for ZnS, FeS and (Zn,Fe)S obtained under the same conditions are given for the comparison in Fig. 2.

Mössbauer spectres at characteristic temperatures: starting sample, 773, 973, 1073 and 1273 K are given in Fig. 3, results of the electronic microanalysis are shown in Fig. 4.

Obtained results given in Fig. 3 show two quasipolar peaks, which correspond to the presence of FeS and ZnS in marmatite. On spectres (2–5), peaks which correspond to marmatite are progressively disappearing. It has to be noticed that the area of the first peak (FeS) rapidly reduces, because the sulfur from FeS is set apart as $SO_2$ gas, while released iron makes the bond Fe–Zn–Fe. This bond in the presence of oxygen form $ZnFe_2O_4$, as can be seen from spectres (2–5).

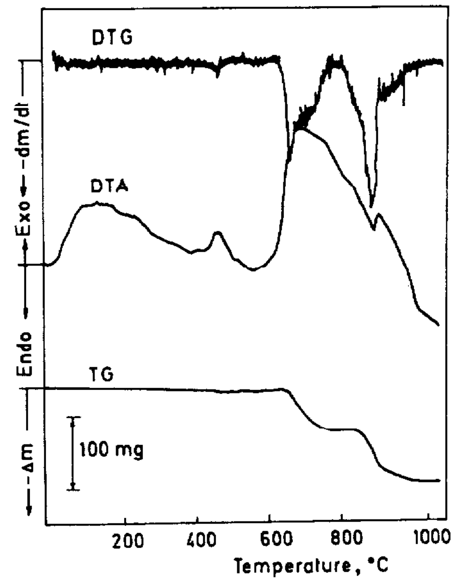

**Fig. 1** DTA-TG-DTG curves for $(0.29Fe\cdot 0.71Zn)S$ (air atmosphere, $\Phi = 10°C\ min^{-1}$)

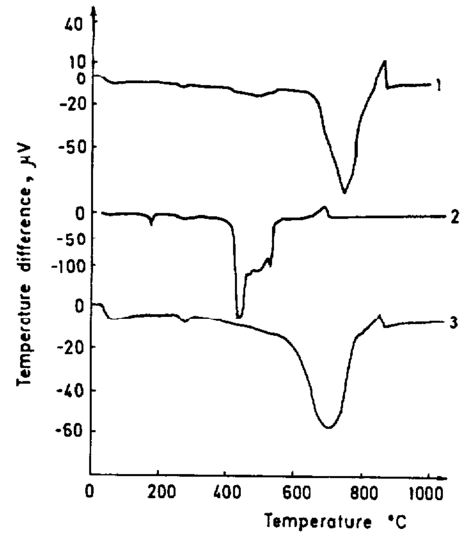

Fig.2 DSC curves for (0.29Fe·0.71Zn)S (1), FeS (2) and ZnS (3) (air atmosphere, $\Phi$ =10°C min$^{-1}$)

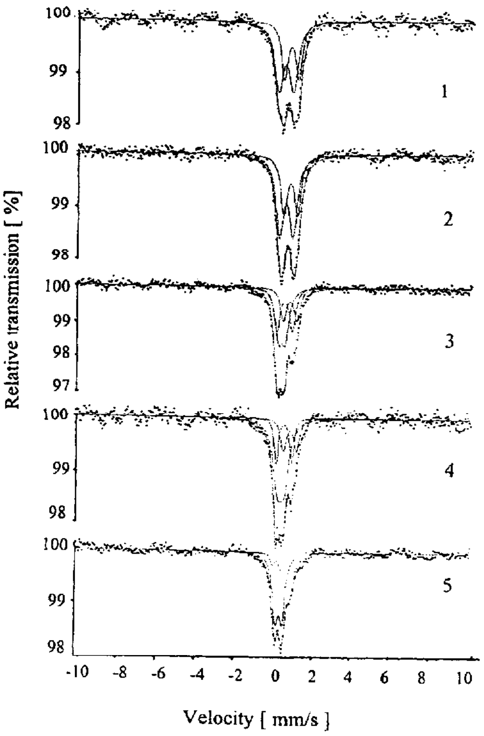

**Fig. 3** Mössbauer spectres for starting sample at room temperature (1), at 773 K (2), 973 K (3), 1073 K (4) and 1273 K (5)

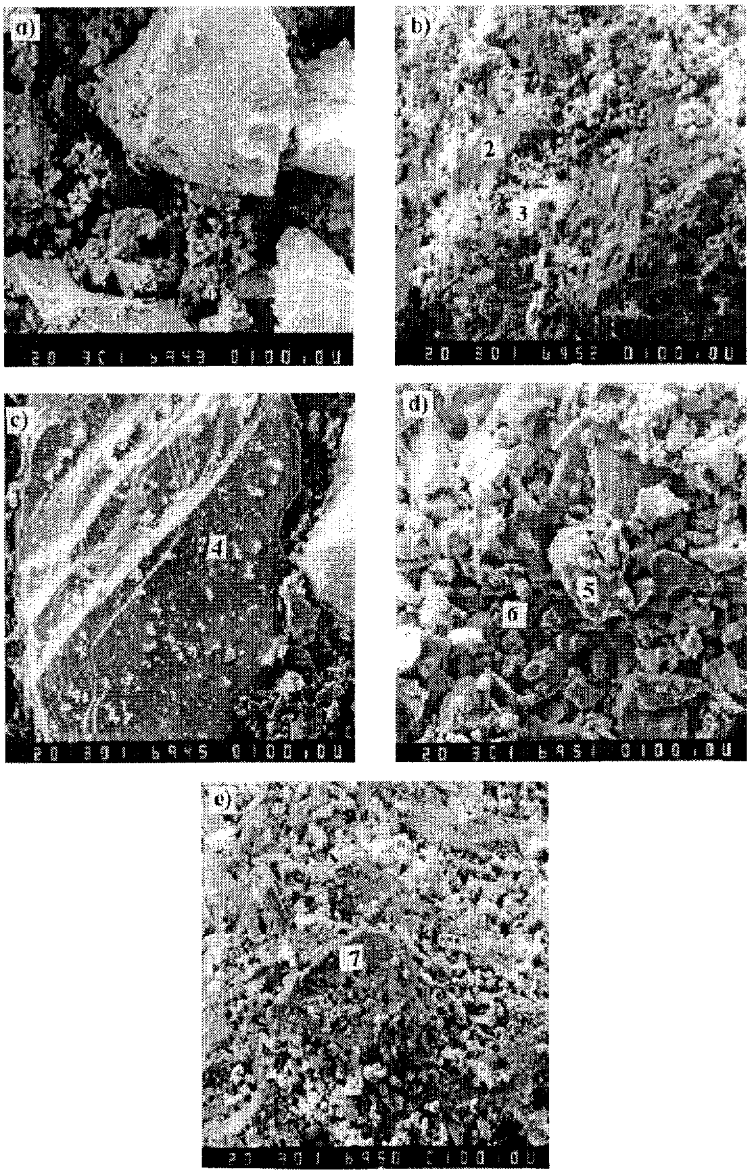

**Fig. 4** Electronic microanalysis results for starting sample at room temperature (1), at 773 K (2), 973 K (3), 1073 K (4) and 1273 K (5)

Based on results shown in Figs 1 and 2, as well as on results obtained by the analysis of the oxidation products at different temperatures given in Figs 3 and 4, the mechanism of the marmatite oxidation process may be presented as follows:

$$3(Zn,Fe)S + 5O_2 = 3ZnS + Fe_3O_4 + 3SO_2 \qquad (1)$$

$$2Fe_3O_4 + 0.5O_2 = 3Fe_2O_3 \qquad (2)$$

$$ZnS + 1.5O_2 = ZnO + SO_2 \qquad (3)$$

The whole mass of the formed $Fe_2O_3$ reacts with ZnO and make zinc ferrite:

$$ZnO + Fe_2O_3 = ZnFe_2O_4 \qquad (4)$$

In the case of the investigated marmatite $0.29Fe{\cdot}0.71ZnS$, 27% Zn of the starting zinc content in marmatite transit to $ZnFe_2O_4$, and 73% Zn to ZnO, which is calculated based on the stoichiometry of Eqs (1)–(4).

Kinetic investigations of the marmatite oxidation process under isothermal conditions and with air as an oxidant, were done for two temperature intervals: first, from 823 to 973, and the second, from 1023 to 1173 K. By kinetic results treatment, it was determined that investigated process in the first temperature interval 823–973 K can be described by the kinetic function: $1-(1-\alpha)^{1/3} = kt$, and in the second temperature interval 1023–1173 K by the kinetic function: $[-\ln(1-\alpha)]^{1/2} = kt$. Arrhenius diagram for both processes is shown in Fig. 5.

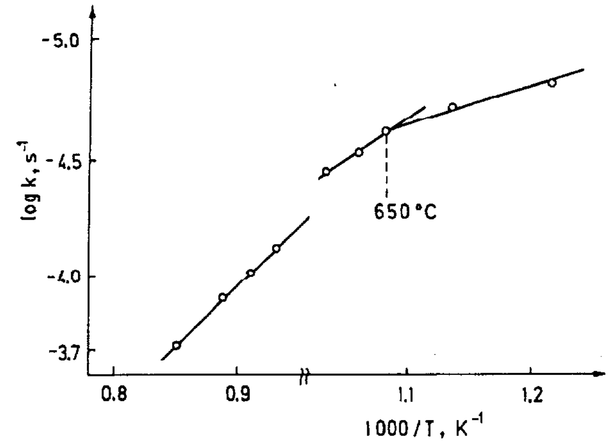

**Fig. 5** Arrhenius diagram for the marmatite oxidation process

It can be pointed out from Fig. 5 that there is a reaction mechanism change at 923 K for the investigated process in the temperature interval 823–973 K. FeS oxidation process, which has the enthalpy change of −116 J g$^{-1}$ (according to DSC measurements) and the activation energy of 31 kJ mol$^{-1}$, transits into the diffusion area with the activation energy of 7 kJ mol$^{-1}$ at temperature 923 K, because the canals for the $SO_2$ gas separation through the pores of the marmatite particles are growing (Fig. 4c).

Starting marmatite grain (Fig. 4a, spot 1) is decreasing its size during the time (Fig. 4b, spot 2 and 3), and at 973K – after FeS oxidation is finished, the pores formed by $SO_2$ gas evolving, appear at the surface of the starting marmatite grain (Fig. 4c, spot 4). With the heating of the sample, at temperature 1073 K grains of formed $ZnFe_2O_4$ appears (Fig. 4a, spot 5 and 6), but during the further heating decrease of their size is noticed (Fig. 4e, spot 8). Also, small quantities of rest marmatite could be registered (Fig. 4e, spot 7), which shows that under the stationary conditions, marmatite oxidation process could not be done completely.

For the oxidation process of ZnS in the temperature interval 1023–1173 K, the enthalpy change was determined $-1710$ J $g^{-1}$ (according to DSC measurements) as well as the activation energy 96 kJ $mol^{-1}$, characteristic for the processes in the kinetic area. Evidently, the starting marmatite grains are cut up in smaller pieces because of the previous oxidation of FeS and $Fe_3O_4$ into $Fe_2O_3$, so larger surface for the contact of ZnS with the oxygen form air is made.

By further heating – after ZnS oxidation, reaction of $ZnFe_2O_4$ formation (Eq. (4)) is taking part, and the value of enthalpy change measured by DSC is 148 J $g^{-1}$.

In the structure of the roast – product of the marmatite oxidation, primary crystals of ZnO and the agglomerate of small $ZnFe_2O_4$ crystals are present. The presence of $ZnFe_2O_4$ crystals is noticed on spectrum (5) in Fig. 3. This is in the accordance with DSC results, which show that intensive unrolling of reaction (4) starts at temperature higher than 1073 K.

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