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Thermochimica Acta 380 (2001) 37–41

thermochimica
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Mössbauer spectroscopy study on the oxidation of sulfide zinc concentrate rich in marmatite

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Received 20 February 2001; accepted 11 June 2001

Abstract

The process of oxidation of sulfide zinc concentrate containing larger quantities of iron (in the form of pyrite and marmatite) is studied through thermal treatment in a stationary layer and air atmosphere. The following methods of study are used: Mössbauer spectroscopy, X-ray diffraction analysis, DTA and TG, chemical analysis, etc.

Mössbauer spectroscopy was used to keep track of the presence and changes in the content of the following phases: FeS_2, mZnS·nFeS, $CuFeS_2$, $FeSO_4$, Fe_2O_3 and $ZnFe_2O_4$ in the initial concentrate and in the products of its oxidation at different temperatures.

Conclusions are made about the influence of roasting temperature on the content of the different iron-containing phases in the oxidation products.

Keywords: Mössbauer spectroscopy; Oxidation; Zinc concentrate; Marmatite; Phase composition

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1. Introduction

The present paper presents a part of our studies into the thermodynamics, kinetics and mechanism of ZnS oxidation [1–4] and the optimization of zinc concentrate roasting in fluid bed [5–8].

A number of studies have been made on the oxidation of metal sulfides [9–17] and roasting of sulfide zinc concentrates [8,18]. DTA, TG, X-ray diffraction analysis, and chemical analysis are usually used.

There is a limited number of studies on the oxidation of marmatite [3,15] and non-standard zinc concentrates rich in iron [8,16,19].

The present study aims at tracing the distribution of iron-containing phases while roasting sulfide zinc concentrate containing larger quantities of iron. The complex composition of the Zn–Fe–S–O system requires the application of various methods of study in order to clarify the mechanism of the processes which take place during the thermal treatment.

2. Experimental

The study was carried out using sulfide zinc concentrate rich in iron with the following chemical composition (in mass %): Zn — 32, Fe — 14, S — 32, Cu — 3.86, Pb — 1.2, SiO_2 — 1.3, etc., and size of the particles: — $100 + 80\,\mu m$.

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PII: S0040-6031(01)00638-4

The zinc concentrate samples were roasted in stationary layer and air flow for 60 min at temperatures 550, 750, 1000°C.

The Mössbauer spectra were taken by means of a standard spectrometer at constant acceleration and room temperature. A 70 mCi ^{57}Co (Gr) source was used. The isomer shifts are given relative to that of α-Fe at room temperature. The experimentally obtained spectra were analyzed using standard software for fitting based on the least-squares method. The parameters of hyperfine interactions such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (H_{eff}) were determined. The relative shares (I, %) of the different spectrum components were determined from the intensities of the corresponding lines. The identification of the various phases was based on the data from references [20–22] and the Mössbauer spectra of FeS_2, $CuFeS_2$, FeS and mZnS·nFeS were taken down by us.

X-ray diffraction analysis was carried out using TUR-M 61 diffractometer (Germany) with a copper or cobalt lamp and an iron filter. DTA and TG were carried out using a Derivatograph Q manufactured by the Hungarian company MOM. The analyses were made under static conditions in air atmosphere and at a heating rate of 10°C min^{-1}. The following sensitivities were used: DTA, 0.5 mV; DTG, 1 mV; TG, 50 mg. The sample mass was 100 mg. A platinum crucible and Al_2O_3 as an inert substance was used.

The chemical analysis was carried out using the methodology described in [23].

The atom-absorption analysis was carried out by a PerkinElmer 4100 device.

3. Results and discussion

The Mössbauer spectra of synthetic FeS and natural minerals are taken down: pyrite, FeS_2; chalcopyrite, $CuFeS_2$ and marmatite, mZnS·nFeS (Fig. 1). Data for hyperfine interactions (IS, QS and H_{eff}) are obtained from them (Table 1). They are used for comparison with data from other sources and the data from our analysis of the Mössbauer spectra of zinc concentrate and the products of its oxidation at different temperatures (Fig. 2).

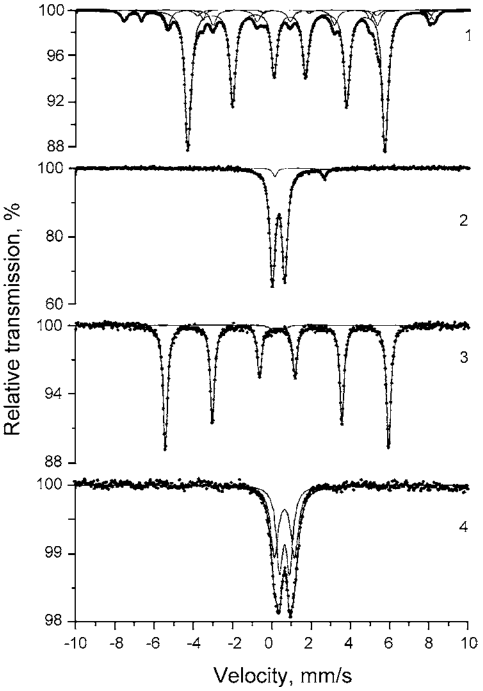

Fig. 1. Mössbauer spectra of: (1) FeS; (2) FeS_2; (3) $CuFeS_2$; (4) mZnS·nFeS.

The Mössbauer spectrum of the initial concentrate (Fig. 2(1)) contains one sextet corresponding to $CuFeS_2$ and three doublet spectra, the first of which corresponds to the pyrite phase and the other two to the marmatite one. The Mössbauer parameters and the relative intensity of the lines of these phases are shown

Table 1
Mössbauer parameters of the studied minerals

No.	Minerals	IS, mm/s (±0.007)	QS, mm/s (±0.007)	H_{eff}, kOe (±0.7)
1	FeS (synthetic)	0.754	−0.075	311.0
2	FeS_2 (pyrite)	0.301	0.626	0
3	$CuFeS_2$ (chalcopyrite)	0.245	−0.001	353.4
4	mZnS·nFeS (marmatite)	$\delta_1 = 0.649$	0.515	0
		$\delta_2 = 0.641$	1.022	0

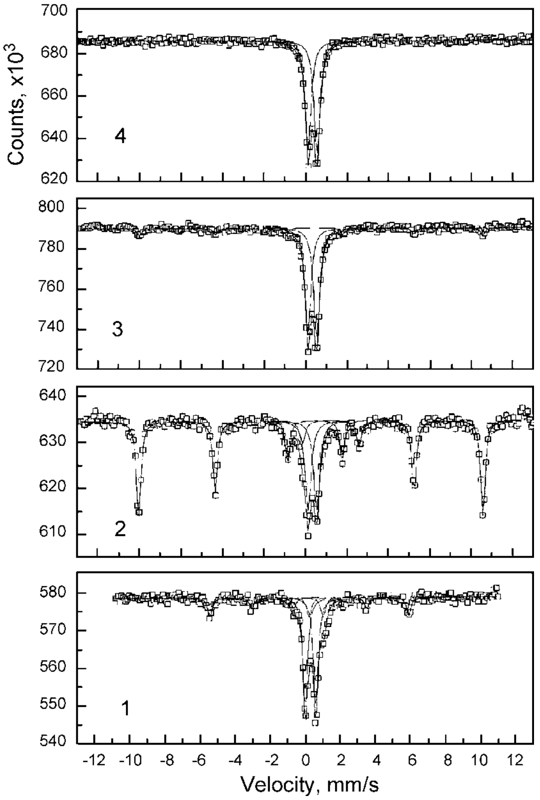

Fig. 2. Mössbauer spectra of initial zinc concentrate (1); roasted at: 550°C (2); 750°C (3); 1000°C (4).

in Table 2. For the purposes of comparison, the table also presents the relative content I_{ch} obtained through chemical analysis. The data in Table 2 show that the prevailing iron-containing phase in the concentrate is FeS_2 (58%). The content of marmatite (27%) is higher than that in the standard zinc concentrates processed. The iron-containing $CuFeS_2$ phase (14.7%) ranks third.

Other authors [17] using X-ray diffraction analysis detect only the presence of marmatite and chalcopyrite in the marmatite concentrate.

Our data are made complete by the X-ray diffraction analysis carried out. It detects the presence of β-ZnS, SiO_2 (α-quartz), PbS in the concentrate as well.

DTA and TG analyses [8] display an intensive exothermal effect at a temperature of 460°C due to the oxidation of FeS_2 and $CuFeS_2$. In our previous studies [24], the following maximums of the DTA curves have been detected: in pyrite oxidation, 480°C and in chalcopyrite oxidation, 500°C. These processes in the marmatite concentrate oxidation result in a small decrease of the mass of the sample. This can be explained by the processes taking place until oxides are obtained.

The Mössbauer spectrum of concentrate oxidized at 550°C (Fig. 2(2)) shows the presence of α-Fe_2O_3 (66%), $FeSO_4$ (8%), $ZnFe_2O_4$ (20%) and residual quantities of the initial iron-containing sulfides: FeS_2 (1%) and mZnS·nFeS (6%).

β-ZnS and zinc sulfate are also detected in the oxidized sample through X-ray diffraction analysis.

The exothermal effects at 670 and 750°C [8] are due to the oxidation of marmatite and β-ZnS. In a previous study of ours [24], the detected maximums of the peaks are at the temperatures of 600 and 740°C, respectively. In the course of marmatite concentrate oxidation, these exothermal effects are connected with an increase in the mass of the sample which proves the formation of sulfates under the conditions of the experiment. With the increase of temperature to about 900°C, the sulfates formed dissociate into oxides and SO_2.

With the increase of oxidation temperature to 750°C (Fig. 2(3)), a considerable decrease in the intensity of α-Fe_2O_3 sextet (11%) is noticed. The doublet of $FeSO_4$ is not detected. In the Mössbauer spectrum, the doublet characteristic of $ZnFe_2O_4$ prevails (89%); it can also contain ions of admixtures (Cu, Cd, Mg, etc.). Intensive ferrite formation takes place at this temperature as a result of the interaction between the previously formed ZnO and Fe_2O_3. The X-ray diffraction analysis detects also free ZnO, resulting from the oxidation of sphalerite, and zinc sulfate too.

The Mössbauer spectroscopy of samples oxidized at 1000°C (Fig. 2(4)) detects only the iron-containing phase $ZnFe_2O_4$. The X-ray diffraction analysis shows free ZnO too.

The data from the chemical analysis (Table 2: I_{ch}, %) confirm the results from the Mössbauer spectroscopy.

The additional studies on the behavior of the powdery samples in the field of a constant magnet show that in samples 1, 2 and 3 (Table 2), a considerable part of the particles (∼60%) demonstrate magnetic properties. They can be isolated as a separate magnetic fraction. Such a fraction is not detected in sample 4 which is oxidized at 1000°C.

Table 2
Mössbauer parameters of the studied samples and results from chemical phase analysis[a]

Sample	Parameter	Phase						Error ±
		FeS_2	$CuFeS_2$	mZnS·nFeS	$FeSO_4$	Fe_2O_3	$ZnFe_2O_4$	
1 (initial)	IS, mm/s	0.314	0.24	0.64 (average)				
	QS, mm/s	0.603		0.79 (average)				0.02
	H_{eff}, kOe		352					0.8
	I, %	58	14.7	27				1
	I_{ch}, %	58.6	41.4					
2 (550°C)	IS, mm/s	0.314		0.64 (average)	1.23	0.36	0.35	0.01
	QS, mm/s	0.603		0.79 (average)	2.74	−0.19	0.36	0.02
	H_{eff}, kOe					516		0.8
	I, %	1		6	8	66	20	1
	I_{ch}, %	0.3		5.7	7.3	68.3	18.4	
3 (750°C)	IS, mm/s					0.36	0.34	0.01
	QS, mm/s					0.18	0.36	0.02
	H_{eff}, kOe					514		0.8
	I, %					11	89	1
	I_{ch}, %					11.8	88.2	
4 (1000°C)	IS, mm/s						0.34	0.01
	QS, mm/s						0.36	0.02
	H_{eff}, kOe							0.8
	I, %						100	1
	I_{ch}, %						100	

[a] I_{ch}-mass content obtained by chemical phase analyses of iron compounds.

The dust particles (sample 2) contain a large quantity α-Fe_2O_3. In pure condition, this oxide has an antiferromagnetic structure. The magnetic behavior of the sample shows that in the present case, this oxide is apparently non-stoichiometric, especially along the contours of the particles. As a result of this, the compensation of magnetic moments in the antiferromagnetic structure is disturbed.

The results from our investigations do not support the marmatite oxidation mechanism proposed in [18]. We do not detect the presence of Fe_3O_4 in the oxidation products. If this oxide exists in the samples, it must be in a very small quantity which is undetectable through Mössbauer spectroscopy and X-ray diffraction analysis.

The studies we have done [4] with plate samples of sphalerite rich in iron (Zn,Fe)S by using optical and scanning microscopy (SEM and SEI) show that at a temperature of 1000°C and a 60 min duration of the oxidation process, an oxide–ferrite crust is formed which contains zincite — ZnO and franclinite — $ZnFe_2O_4$. The considerable decrease (∼30%) in the volume of the obtained product (ZnO and $ZnFe_2O_4$) compared to the initial phase (Zn,Fe)S while the shape and size of the particle is preserved results in obtaining a highly porous and laminated oxide–ferrite product.

4. Conclusions

Mössbauer analysis in combination with X-ray diffraction analysis, DTA, TG and chemical analyses make possible the thorough investigation of the processes taking place during the thermal treatment in air atmosphere of zinc concentrates with high content of iron. Data are obtained about the content of different iron-containing phases in the intermediate and final products of roasting. This is of great interest for studying the mechanism of oxidation and ferrite formation. The results obtained can be used successfully in preparing mixtures of such raw materials and in their further metallurgical processing.

Acknowledgements

A part of the results of this study was presented at the Second International Conference of the Chemical Societies of the South-Eastern European Countries — Chemical Sciences for Sustainable Development, June 6–10, 2000, Halkidiki, Greece.

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