

THERMODYNAMIC AND KINETIC ANALYSIS OF THE Cu-Fe-S SYSTEM OXIDATION PROCESS

N. Štrbac¹, I. Mihajlović, D. Živković, Ž. Živković, B. Anđelić*

Technical Faculty Bor, University in Belgrade,
Vojske Jugoslavije 12,
19210 Bor, Serbia and Montenegro
*Copper Institute Bor, Zeleni bulevar 35,
19210 Bor, Serbia and Montenegro
E-mail: nstrbac@tf.bor.ac.yu

Received 16 December 2005
Accepted 20 February 2006

ABSTRACT

In this paper results of experimental investigations of the oxidation process of copper minerals (chalcopyrite and bornite) as well as copper matte in the air atmosphere are presented. Thermodynamic parameters of the investigated processes in the system Cu - Fe - S were defined using X-Ray analysis and DTA-TG-DTG results.

The activation energy of the studied processes was determined using Sharps method of half time of reaction under isothermal conditions.

For the experimental investigations copper minerals: bornite and chalcopyrite from the Bor copper mine, as well as copper matte from the Bor smelter plant were used.

Keywords: activation energy, DTA-TG-DTG, oxidation, sulfides, RDA analysis.

INTRODUCTION

Physical and chemical characteristics of sulfide minerals and concentrates as well as their behavior during heating (oxidative roasting) are parameters that should be known in order to control number of processes of nonferrous metals extraction [1,2].

Results of investigations of sulfide combustion temperatures (start of desulfurization process) [3,4], with kinetic and mechanism of some pure sulfides dissociation [5,6] are present in literature. Studying of copper matte and mattes from the system Cu-Fe-S, in general, was also subject of interest for many researchers from the theoretic as well as practical aspect [7, 8].

EXPERIMENTAL

For the experimental investigations the natural minerals chalcopyrite and bornite from Bor copper mine as well as copper matte from Bor copper smelter obtained during classical smelting process in a reverberatory furnace were used. The chemical composition of the samples used from the aspect of Cu, Fe and S content was:

- chalcopyrite: Cu-21,25; Fe-29,76; S-29,14 and remaining 19,85 %;
- bornite: Cu-55; Fe-14,10; S-25,59 and remaining: 5,31 %;
- copper matte: Cu-37,50; Fe-23,70; S-32,47 and remaining: 6,33 %.

The thermal analyses were performed using Derivatograph 1500 (MOM Budapest) under the following conditions: air atmosphere, heat rate 10 °/min and $T_{\max}=1000^{\circ}\text{C}$. For the mineralogical characterization of the starting samples a Siemens apparatus was used with Cu-anti-cathode with 20 mA current and voltage of 40 kV. Heating of the investigated samples at isothermal conditions was performed in Mars's (electro resistant) furnace. The distinct amount of air was introduced into the reaction area, while gaseous product of reaction (mostly SO_2) was generated from the tube to the absorption tanks filed with aqueous solution of hydrogen peroxide thus producing sulfuric acid. Then the acid in the presence of an indicator was reacted with measured standard solution of sodium hydroxide for the purpose of calculation of sulfur insulated content as well as the degree of desulphurization during the oxidation roasting.

RESULTS AND DISCUSSION

The mineralogical composition of the investigated samples was determined using X-Ray analysis. The results obtained show that copper in the chalcopyrite sample occur as mineral chalcopyrite with some amount of quartz. In the bornite sample copper is present as mineral bornite with some amount of calcite. In copper matte copper is present as elemental copper, bornite and delafosite with some amount of magnetite.

The results obtained in isothermal conditions describing degree of desulfurization dependence on time at different temperatures $\alpha = f(t)$ were the starting data for the kinetic analysis according to the method of H.J. Sharp [14].

Chalcopyrite

The kinetic analysis according to the results at DTA curve should be done in two temperature intervals. In the first temperature interval starting chalcopyrite samples were heated at temperatures 350 - 550°C during 30 minutes, and in the second temperature interval samples were heated at 575-700°C. Analyzing those samples the degree of the desulfurization and its dependence on the time and the temperature was determined (Fig. 1).

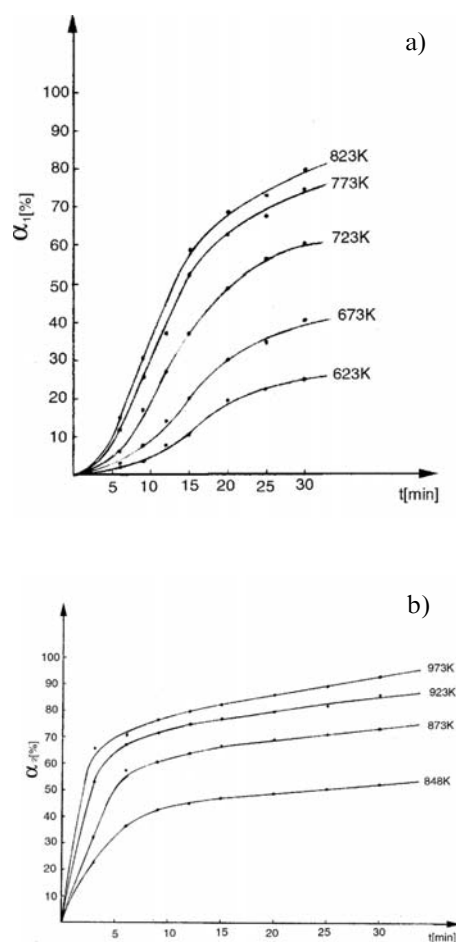


Fig. 1. Degree of desulfurization dependence on time at different temperatures of chalcocite sample roasting: a) first temperature interval; b) second temperature interval.

For the kinetic parameters calculation Sharps method of half time of reaction was used. It is based on the determination of the reaction mechanism from the experimental data $\alpha = f(t)$ by using the reduced half time diagram in the form of $F(\alpha) = f(t/t_{0,5})$, where: $t_{0,5}$ is the half time of reaction and α is the degree of reaction.

To determine the kinetic function $F(\alpha)$ which approximate experimental results the best comparison of the experimental data for the first temperature interval with functions presented in Table 1 was done. The experimental curve was closest to the function A_2 : $[-\ln(1-\alpha)]^{1/2} = k \cdot t$; while for the second tempera-

Table 1. Equations for kinetic models defined by H.J.Sharp [14].

Function	Equation	Process that define rate of reaction
D ₁	$\alpha^2 = k \cdot t$	Linear diffusion
D ₂	$(1-\alpha)\ln(1-\alpha)+\alpha = k \cdot t$	Two-dimensional diffusion, cylindrical symmetry
D ₃	$[1-(1-\alpha)^{1/3}]^2 = k \cdot t$	Tree-dimensional diffusion, Spherical symmetry, Jander`s Equation
D ₄	$(1-2/3\alpha)-(1-\alpha)^{2/3} = k \cdot t$	Tree-dimensional diffusion, Spherical symmetry, Ginstling – Braunstin equation
F ₁	$-\ln(1-\alpha) = k \cdot t$	Randomly formation of new phase nucleus, one nucleus per one particle
A ₂	$[-\ln(1-\alpha)]^{1/2} = k \cdot t$	Randomly formation of new phase nucleus, Avrami equation (I)
A ₃	$[-\ln(1-\alpha)]^{1/3} = k \cdot t$	Randomly formation of new phase nucleus, Avrami equation (II)
R ₂	$1-(1-\alpha)^{1/2} = k \cdot t$	Reaction at the phase boundary, cylindrical symmetry
R ₃	$1-(1-\alpha)^{1/3} = k \cdot t$	Reaction at the phase boundary, spherical symmetry

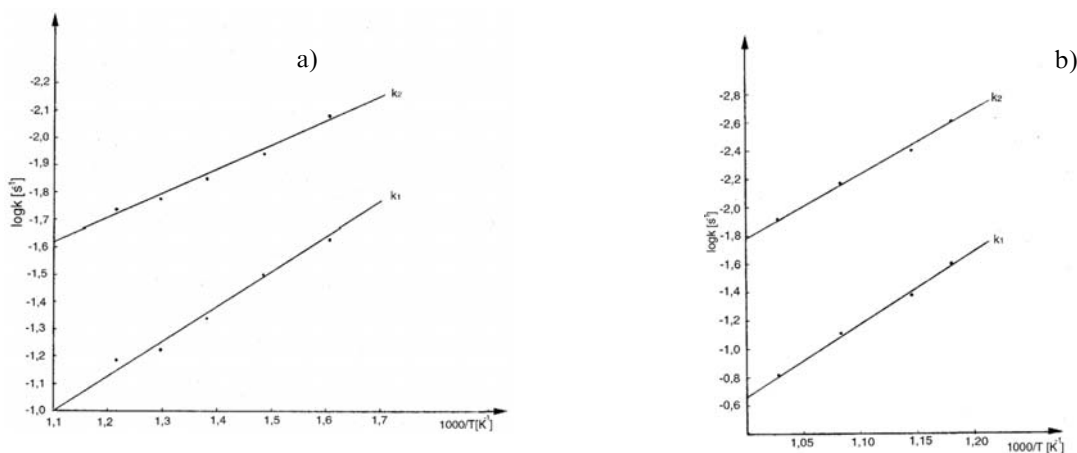


Fig. 2. Arrhenius diagram for the process of chalcopyrite oxidation: a) first temperature interval, b) second temperature interval.

ture interval it was: R₃: $1-(1-\alpha)^{1/3} = k \cdot t$. Using chosen kinetic equations the linearization of the experimental results was done for both temperature intervals. The linearized isotherms obtained had inflections for both temperature intervals which indicate change of the process regime. From the gradient of the isotherms linearized, the rate constants (k_1 and k_2) were determined for chalcopyrite oxidation at different temperatures for both periods. Using this values Arrhenius diagrams were constructed (Fig. 2).

Using Arrhenius diagrams, the activation energy was also calculated. The kinetic parameters of the investigated process are presented in Table 2.

Bornite

Calculation of the kinetic parameters for bornite sample was performed using the same procedure as described above for the chalcopyrite experiment. Since most desulfurization in the first temperature interval happens on 550°C and equals 39 %, it means that it was not possible to use reduced half time method since degree of 50 % is not obtained. In the second temperature interval the highest degree of desulfurization is 89,22 %.

To determine kinetic function $F(\alpha)$ which models process in first temperature interval it is necessary to linearize the experimental results with all functions from Table 1 and to chose one which gives the

Table 2. Kinetic parameters for chalcopyrite oxidation process.

I temperature interval	Ea, kJ/mol	Until the fraction	25	Diffusion area
		After the fraction	17	
	Rate constant, 1/s	Until the fraction	$k_1 = 10,47 \cdot 10^{-2} \cdot \exp\left(\frac{-2959}{T}\right)$	
		After the fraction	$k_2 = 2,39 \cdot 10^{-2} \cdot \exp\left(\frac{-1997}{T}\right)$	
Kinetic equation	Until the fraction	$[-\ln(1-\alpha)]^{1/2} = 10,47 \cdot 10^{-2} \cdot \exp\left(\frac{-2959}{T}\right) \cdot t$		
	After the fraction	$[-\ln(1-\alpha)]^{1/2} = 2,39 \cdot 10^{-2} \cdot \exp\left(\frac{-1997}{T}\right) \cdot t$		
II temperature interval	Ea, kJ/mol	Until the fraction	98	Kinetic area
		After the fraction	86	
	Rate constant, 1/s	Until the fraction	$k_1 = 21,88 \cdot 10^{-2} \cdot \exp\left(\frac{-11777}{T}\right)$	
		After the fraction	$k_2 = 1,66 \cdot 10^{-2} \cdot \exp\left(\frac{-10350}{T}\right)$	
Kinetic equation	Until the fraction	$1 - (1-\alpha)^{1/3} = 21,88 \cdot 10^{-2} \cdot \exp\left(\frac{-11777}{T}\right) \cdot t$		
	After the fraction	$1 - (1-\alpha)^{1/3} = 1,66 \cdot 10^{-2} \cdot \exp\left(\frac{-10350}{T}\right) \cdot t$		

Table 3. Kinetic parameters for the bornite oxidation process.

I temperature interval	Ea, kJ/mol	Until the fraction	55	Kinetic → Diffusion area
		After the fraction	13	
	Rate constant, 1/s	Until the fraction	$k_1 = 46,22 \cdot \exp\left(\frac{-6515}{T}\right)$	
		After the fraction	$k_2 = 8,74 \cdot 10^{-3} \cdot \exp\left(\frac{-1564}{T}\right)$	
Kinetic equation	Until the fraction	$1 - (1-\alpha)^{1/3} = 46,22 \cdot \exp\left(\frac{-6515}{T}\right) \cdot t$		
	After the fraction	$1 - (1-\alpha)^{1/3} = 8,74 \cdot 10^{-3} \cdot \exp\left(\frac{-1564}{T}\right) \cdot t$		
II temperature interval	Ea, kJ/mol	Until the fraction	117	Kinetic area
		After the fraction	193	
	Rate constant, 1/s	Until the fraction	$k_1 = 18,05 \cdot 10^4 \cdot \exp\left(\frac{-14138}{T}\right)$	
		After the fraction	$k_2 = 41,09 \cdot 10^8 \cdot \exp\left(\frac{-23158}{T}\right)$	
Kinetic equation	Until the fraction	$-\ln(1-\alpha) = 18,05 \cdot 10^4 \cdot \exp\left(\frac{-14138}{T}\right) \cdot t$		
	After the fraction	$-\ln(1-\alpha) = 41,09 \cdot 10^8 \cdot \exp\left(\frac{-23158}{T}\right) \cdot t$		

best linearization. On this way kinetic equation R3: $1 - (1-\alpha)^{1/3} = k \cdot t$, was chosen. For the second temperature interval function F_1 : $-\ln(1-\alpha) = k \cdot t$ was chosen using Sharps method of reduced half time of reaction. Using those results Arrhenius diagrams for the bornite oxidation process were constructed. Then the kinetic parameters of the investigated process were determined (Table 3).

Copper matte

The same experimental procedure was conducted for the copper matte sample. Using results presenting the degree of desulfurization dependence on the time and the temperature, and procedure discussed above kinetic equations for investigated process were determined. For the first temperature interval kinetic equation is F_1 : $-\ln(1-\alpha) = k \cdot t$ and for the second tem-

Table 4. Kinetic parameters for the process of copper matte oxidation.

I temperature interval	Ea, kJ/mol	Until the fraction	55	Kinetic area
		After the fraction	39	
	Rate constant, 1/s	Until the fraction	$k_1 = 180.717 \cdot \exp\left(\frac{-6615}{T}\right)$	
		After the fraction	$k_2 = 2.655 \cdot \exp\left(\frac{-2654}{T}\right)$	
	Kinetic equation	Until the fraction	$-\ln(1-\alpha) = 180.717 \cdot \exp\left(\frac{-6615}{T}\right) \cdot t$	
		After the fraction	$1 - (1-\alpha) = 2.655 \cdot \exp\left(\frac{-2654}{T}\right) \cdot t$	
II temperature interval	Ea, kJ/mol	Until the fraction	68	Kinetic area
		After the fraction	52	
	Rate constant, 1/s	Until the fraction	$k_1 = 132.129 \cdot \exp\left(\frac{-8179}{T}\right)$	
		After the fraction	$k_2 = 2.037 \cdot \exp\left(\frac{-6254}{T}\right)$	
	Kinetic equation	Until the fraction	$1 - (1-\alpha)^{1/2} = 132.129 \cdot \exp\left(\frac{-8179}{T}\right) \cdot t$	
		After the fraction	$1 - (1-\alpha)^{1/2} = 2.037 \cdot \exp\left(\frac{-6254}{T}\right) \cdot t$	

perature interval equation $R_2: 1 - (1-\alpha)^{1/2} = k \cdot t$, was chosen. Using Arrhenius diagrams for the process of copper matte oxidation the kinetic parameters were calculated (Table 4).

CONCLUSIONS

In this paper the results for the thermodynamics and the kinetic investigations for the process of mineral chalcopyrite and bornite as well as copper matte oxidation process are presented. The kinetic parameters of the investigated process were determined using Sharps method of reduced half time of reaction. Using defined kinetic parameters the model equations for all three investigated samples were proposed. Results obtained according to the DTA analysis suggested that oxidation process should be analyzed in two temperature intervals. From the values for the activation energy it can be concluded that the process of chalcopyrite oxidation is carried out in the diffusion area during the first temperature interval, and in the kinetic area during the second. The process of mineral bornite oxidation starts in kinetic and moves to diffusion area, during the first and is carried out in the kinetic area during the second temperature interval. For the copper matte sample ox-

idation process is carried out in the kinetic area during both temperature intervals.

REFERENCES

1. A.V. Vanyukov, V. Zaitsev, Theory of the Pyrometallurgical Processes, Metalurgia, Moscow, 1973, (in Russian).
2. Ž.D. Živković, V. Savović, Theory of the Pyrometallurgical Processes, Bor, 1994, (in Serbian).
3. R. Dimitrov, A. Hekimova, S. Asenov, T. Ruskov, T. Tomov, Thermochim. Acta, **40**, 1980, 349.
4. R. Dimitrov, B. Boyanov, Thermochim. Acta, **64**, 1983, 27.
5. Ž.D. Živković, N. Milosavljević, J. Sestak, Thermochim. Acta, **157**, 1990, 215.
6. T. Karvan, C. Malinovski, Thermochim. Acta, **17**, 1976, 195.
7. M. Perez-Tello, H. Yong Sohn, K. St. Marie, A. Jokilaakso, Metallurgical and materials transactions B, **32**, 2001, 847.
8. M. Nagamori, A. Yazawa, Canadian Metallurgical Quarterly, **41**, 1997, 175-192.
9. D. Valigham, J. Creig, Mineral chemistry of metal sulfides, Cambridge University Press, Cambridge, 1978.

10. D. Vogah, D. Kreig, Himia sulfidnih mineralov, Mir, Moskva, 1981, (in Russian).
11. V.I. Babushkin et al., Termodinamika silikatov, Stroizdat, Moskva, 1986, (in Russian).
12. M.H. Karapetjanc, Hemicheskaja Termodinamika, Himija, Moskva, 1975, (in Russian).
13. Ž. Živković, Teorija metalurjskih procesa, Bor, 1992, (in Serbian).
14. H.J. Sharp et al., J. Amer. Ceram. Soc., **49**, 1966, 379.
15. V.I. Smirnov, A.J. Tihonov, Objig mednih rudi i koncentratov, Metalurgija, Moskva, 1966, (in Russian).