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THERMODYNAMIC AND KINETIC ANALYSIS OF CADMIUM SULPHIDE OXIDATION PROCESS

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ABSTRACT
This paper presents the results of the cadmium sulfide oxidation roasting process from the thermodynamic and kinetic aspect. Based on the known thermodynamic values for the reactions in the Cd - S – O system, phase stability diagrams were constructed. Kinetic investigations under the non-isothermal conditions have enabled the determination of the kinetic parameters.
Keywords: Cd-sulphide, oxidation, thermodynamic and kinetic analysis

1. INTRODUCTION

Oxidative roasting presents one of the stages of sulphide concentrates pyrometallurgical processing.
G. S. Frenc [1] systematically studied the interaction of a number of metal sulfides with oxygen; the reaction rate and sequence of individual reactions in the Me–S-O system was determined. CdS exists in two allotropic modifications: α (hexagonal) and β (cubic).
The phase transition temperature of the Cd-sulfide from the sphalerite structure type β-CdS into structure of α-CdS wurtzite lies in the temperature range from 973 to 1073 K [2]. Chemistry of the cadmium sulphide oxidation process with oxygen from the air was studied by Adamiano [3]. The influence of the air on the cadmium sulfide shows the following behaviour: at 573 K, the primary oxidation products, sulfates, were detected. Further, at 873 K, CdO was discovered in the reaction products. At 973 K sulfide phase disappeared, while the amount of cadmium oxide was increased. The paper of Moldovanska et. al. [4] presents the results of Cd-sulfide oxidation in non-isothermal conditions.

2. RESULTS AND DISCUSSION

For the experimental investigation the sample of cadmium sulfide was used. The sample was synthesized and prepared at the Department of Inorganic Chemical Technology "Paisiy Hilendarski" in Plovdiv, Bulgaria.
Based on the known thermodynamic values for the reactions that occur in the Cd - S – O system, phase stability diagrams for this system were constructed (Figure 1).

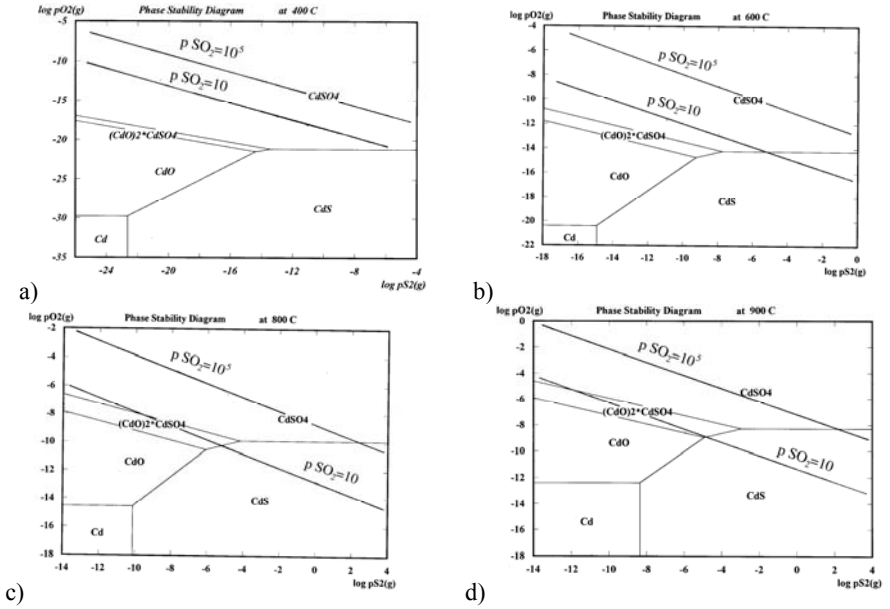

Figure 1. PSD diagrams of the Cd-S-O system at following temperatures:
a) 673 K b) 873 K c) 1073 K d) 1173 K

PSD diagrams present the dependence between log pS_2 – log pO_2, typical for the oxidation process at different temperatures and different pSO_2 values.

Figure 2 shows the DSC analysis results of the cadmium sulfide oxidation in air, at the heating rate of 20 K/min.

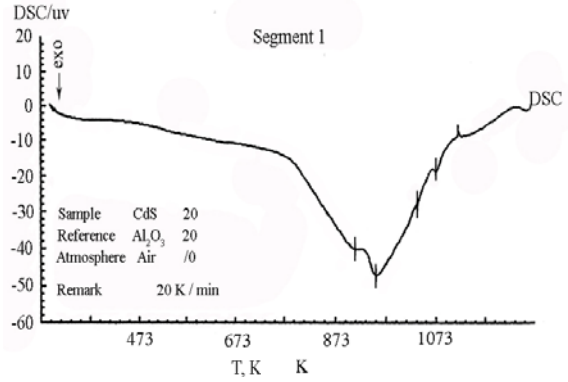

Figure 2. The DSC analysis results of the CdS sample

DSC analysis results showed the presence of four exothermal peaks in the temperature range from 753 to 1073 K, and the occurrence of the endothermal peak at temperatures above 1223 K.
To determine the specific heat changes of the solid reaction products generated during the investigated process, a comparative method was used, which required a duplicate experiment tested with the sample and the standard, which in this case was a sapphire disk. The specific heat calculation for each temperature was carried out by using the following dependency:

$$C_p = \frac{m_{st} \cdot U_s}{m_s \cdot U_{st}} \cdot C_{p_{st}}, J / gK \quad (1)$$

where are: Us – potential difference for the sample, μV; Ust – potential difference for the standard, μV; m_s- mass of the sample, mg; m_{st} -mass of the standard, mg and Cp_{st} -specific heat capacity for the standard (from the literature), J/gK.
The calculated values of Cp according to Equation 1 are shown in Table 1.

Table 1. The dependence between the specific heat capacity and temperature for CdS

Temperature, K	Cp (CdS), J/gK
473	0,164
673	-0,307
873	-8,773
1073	0,815

Based on the results obtained by DTA and DSC, the mechanism of the cadmium sulfide oxidation was assumed. The appearance of four exothermal peaks, followed by alternating mass increase and decrease in the temperature range from 753 to 1073 K corresponds to the oxidation of Cd-sulphide to Cd-sulphates and appropriate oxysulphates, and further, oxides. Occurance of the endothermal peak at temperatures above 1223K indicates a dissociation process of formed cadmiumsulphate into cadmium oxide.
In order to determine the kinetics of the cadmium sulphide oxidation, DSC curves of the samples were obtained. The DSC experiments were performed in the air atmosphere at different heating rates (5 to 30 °/min).
In figure 3 is shown the dependence of the maximum peak temperature T_m in a function of heating rate.

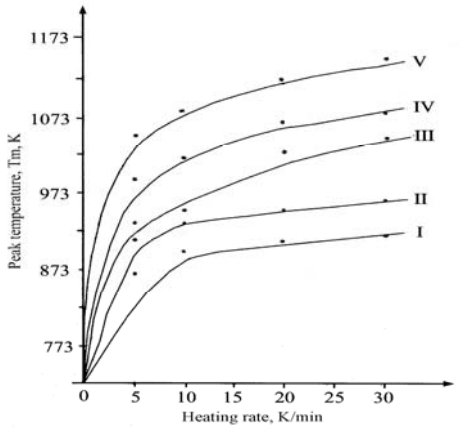

Figure 3. T_m dependence of the heating rate for the processes that occur during the CdS oxidation

Statistical method of least squares was used to calculate the most probable line inclinations, which made possible to determine the activation energy of the investigated process. The intercept on the ordinate gives the value of the integration constant C. The results are shown in Table 2.

Table 2. The calculated values of activation energy and the integration constants of the CdS oxidation process by the H. E. Kissinger method

PROCESS	H. E. KISSINGER	
	Ea, kJ/mol	C
I	220	$1{,}00 \cdot 10^{8}$
II	241	$3{,}30 \cdot 10^{8}$
III	89	$7{,}10 \cdot 10^{-1}$
IV	148	$3{,}30 \cdot 10^{2}$
V	189	$1{,}06 \cdot 10^{4}$

Calculated values of the activation energy suggest that the processes which occur during the cadmium sulfide oxidation process are found in the kinetic domain.

3. CONCLUSIONS

Sulfides can be easily oxidized when heated in the air. Oxidative roasting is one of the stages in the sulphide concentrates pyrometallurgical processing. Sulphides of heavy non-ferrous metals have an important application in the base chemical industry as a raw material for sulfuric acid and its salts production. Semiconductor properties of sulfides have found a practical application for a long time, for example, dielectric diodes and triodes are made from the material based on cadmium sulfide.

Thermal analysis, which was used as a part of the experimental investigation in this paper, showed the changes in mass of the sample, according to the TG curve with the temperature change for Cd sulphide and their corresponding characteristic peaks on the DTA curve. Results of the DTA analysis show occurrence of four exothermal peaks in the temperature range from 753 K to 1073 K. Temperature rising above 1223 K leads to the appearance of one endothermal peak, accompanied by mass loss on TG curve, which indicates a formed cadmium sulfate dissociation into cadmium oxide.

Kinetic analysis was done using the H. E. Kissinger method. The kinetic parameter values were obtained. The calculated activation energy value suggests that the processes which occur during the cadmium sulfide oxidation are found in the kinetic domain.

4. ACKNOWLEDGEMENT:

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