

KINETICS AND MECHANISM OF SYNTHETIC CoS OXIDATION PROCESS

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Abstract

The results of investigation of kinetics and mechanism for synthetic α -CoS oxidation process are presented in this paper. Based on experimental data obtained using DTA and XRD analysis and constructed PSD diagrams for Co-S-O system, mechanism of synthetic α -CoS oxidation process is suggested. Characteristic kinetic parameters were obtained for experimental isothermal investigations of desulfurization degree using Sharp method.

Keywords: cobalt sulfide oxidation, DTA, kinetic investigation.

1. Introduction

Five sulfide phases are affirmed in the Co-S system. Those phases are: $\text{Co}_4\text{S}_{3\pm X}$, Co_9S_8 , CoS_{1+X} , Co_3S_4 and CoS_2 . In the book [1] those phases are confirmed with addition of $\text{CoS}_{1,06-1,17}$ which has nickel-arsenide superstructure. Cobalt (II) sulfide has great importance in metallurgical

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processes. Melting point of this compound is 1455 K and density 5450 kg m⁻³ [2]. In the papers [3,4,5] rhombohedra structure of CoS is reported. However it is wide accepted that compound α -CoS has amorphous structure, especially when synthesized [6]. Although high temperature metallurgy of sulfide ores is a matter of general interest, the oxidation process of cobalt sulfide has not been extensively investigated yet, with the exception of Kowzan *et al.* paper [7] where oxidation of CoS_{1.023} grains in air atmosphere was investigated in temperature range 823-983 K and series of three Asaki *et al.* papers concerning oxidation of nickel sulfide [8], iron sulfide [9] and cobalt sulfide [10]. The authors [7] are comparing their results with Asaki *et al.* [10] results, in retrospective form, which are describing investigation of the CoS grains oxidation processes in a gas stream of mixed oxygen and nitrogen. Experiments were performed at temperatures between 873 and 1123 K with continuous registration of the sample weight change and SO₂ emission. Single rectangular plates of CoS_{1.020-1.105}, 2-mm thick and a few mm long and wide were cut from dense cobalt sulfide ingot and oxidized. In experiments performed at 873 and 923 K an increase of weight of samples in initial stage of oxidation process was found, accompanied by negligible (according to figures presented in the work [10]) evolution of SO₂ and formation of dense layer of oxide (CoO) on the sample surface. Assuming that there was no SO₂ evolution, Asaki *et al.* [10] suggested that diffusion of cobalt from the bulk of sulfide to its surface followed by oxidation of cobalt on the surface was the rate-determining step of oxidation in these initial few minutes of the process. The authors suggested also that in the next stage of oxidation cobalt sulfide was directly oxidized to cobalt oxide (CoO) and SO₂ with decrease of sample weight. No increases of weight of samples at higher temperatures (973, 1023 and 1123 K) were observed and at the same time considerable amounts of SO₂ were emitted. At this stage, direct oxidation of cobalt sulfide to CoO followed by oxidation of CoO to Co₃O₄ was suggested. The formed oxide layers were porous due to evolution of SO₂ gas and oxygen transfer through the porous oxide layer controlled oxidation. In this paper, reaction mechanism to some extent different than those suggested by Asaki *et al.* [10] and Kowzan *et al.* [7] is suggested.

2. Experimental

Samples of synthesized CoS, from University "Paisiy Hilendarsky" Plovdiv (Bulgaria) were used in the investigation. X-Ray analysis was performed in order to characterize investigated samples after oxidative roasting at different temperatures. The phase composition was determined on Siemens X-ray equipment with a Cu anticathode and Ni filter at a voltage 40 kV and current of 18 mA.

Thermal behavior and mass changes analysis of the starting sample, during oxidation in non-isothermal conditions were performed using the results of simultaneous DTA-TG-DTG analysis. For the purpose of the thermal analysis Derivatograph - Q (MOM Budapest) was used at following conditions: air atmosphere, heating rate of 100/min and $T_{max}=1273K$.

Isothermal investigations were performed using standard equipment. Isothermal investigations were performed using an electric resistance furnace with thermostatic control. A measured volume of air was introduced into the reaction area, while gaseous product of reaction (mostly SO_2), were passed from the furnace tube to absorption tubes, filed with an aqueous solution of hydrogen peroxide, producing sulfuric acid. Sulfuric acid produced was reacted with measured standard solution of sodium hydroxide in the presence of indicator for the purpose of calculation of sulfur content and hence the degree of desulfurization during oxidation roasting was calculated with % of errors expected $\pm 0.1\%$.

The degree of desulphurisation was used for determination of the kinetic parameters of oxidation, using Sharp's isothermal model [11] described later.

3. Results and Discussion

3.1. Mechanism of oxidation

Asaki et al. [10] as well as Kowzan et al. did not take into account cobalt sulfate as a co-product of oxidation. However, analysis of Co-S-O predominance phase diagram (e.g., diagrams at 473 and 1273 K, calculated using HSC software [12]-presented in Fig. 1. clearly reveals that cobalt sulfate

should also be considered as a product of sulfide oxidation. Oxidized by air with oxygen pressure of $\log p_{O_2} = -13.4$ cobalt sulfide reacts to CoO (Fig. 1.b), but if partial pressure of SO_2 is high enough the subsequent reaction to cobalt sulfate is possible. With increase of temperature equilibrium lines in Fig. 1 move right and up (there are also some changes within sulfide phases) and area of CoO enlarges. With decrease of temperature, this movement is reversed (left and down); so at moderate temperatures, direct oxidation of sulfide to sulfate is generally possible (Fig.1.a). This possibility is proven in this paper using X-Ray analysis of product of oxidation at 923 K (Fig. 2.a).

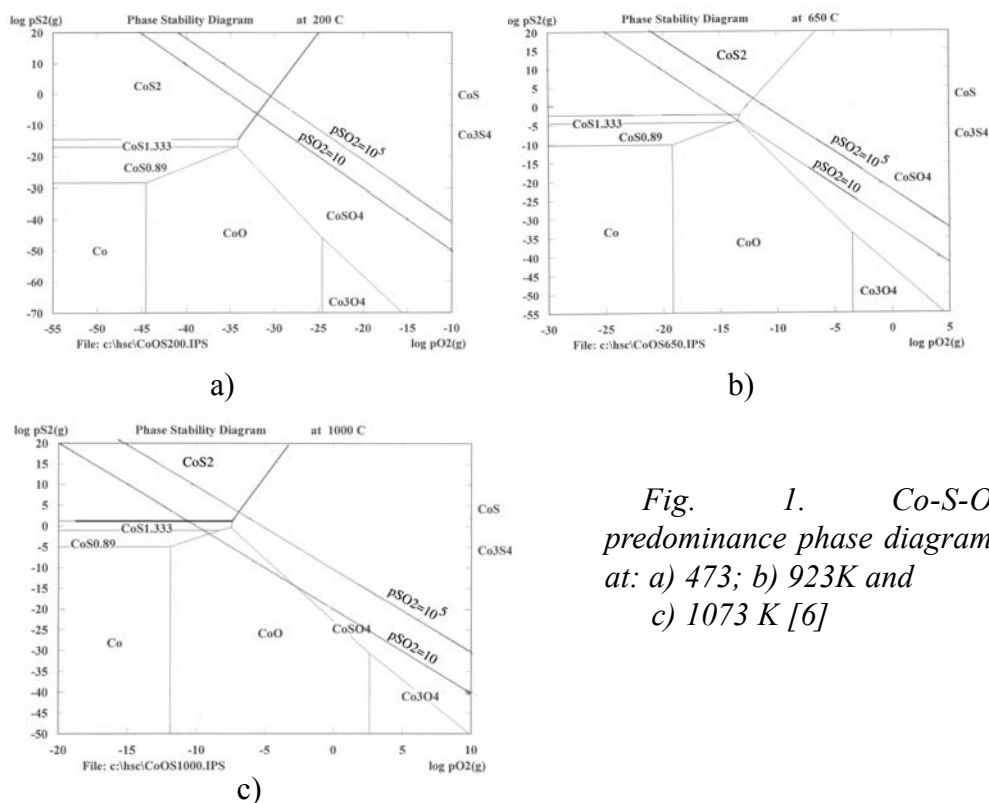


Fig. 1. Co-S-O predominance phase diagram at: a) 473; b) 923K and c) 1073 K [6]

Decomposition of cobalt sulfate should proceed when partial pressure of SO_2 decreases below equilibrium line $CoSO_4/CoO$ (Fig. 1). Thus, cobalt (III) oxide, Co_3O_4 , could be the final product of oxidation, only after CoO is oxidized to Co_3O_4 , according to the PSD diagrams. Still Co_3O_4 is the resulting

outcome of oxidation, in investigated condition of air atmosphere, at 1073, proved by X-Ray analysis presented in Fig. 2.b.

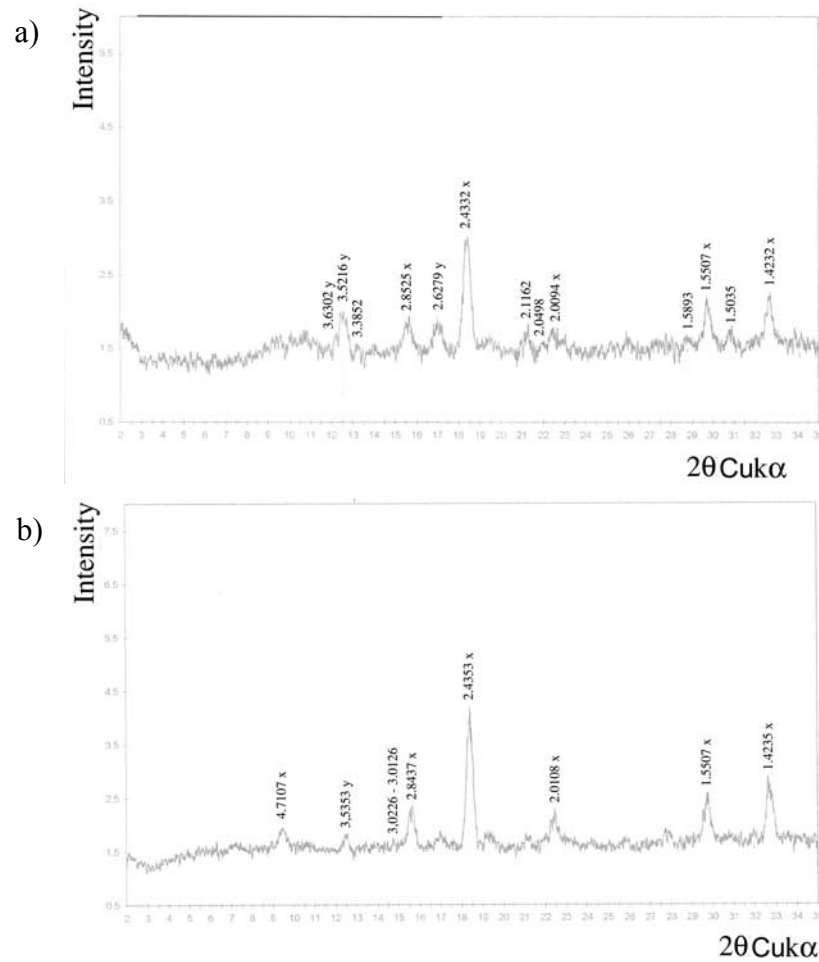


Fig.2. X-Ray patterns of CoS products of oxidation obtained at: a) 923 and b) 1073K, where: x- Co_3O_4 ; y- $CoSO_4$

Results presented above-PSD diagrams, SO_2 evolution rates and X-ray analysis- indicate on mechanism of cobalt sulfide oxidation. Further development of potential mechanism was sustained by DTA results presented in Fig. 3.

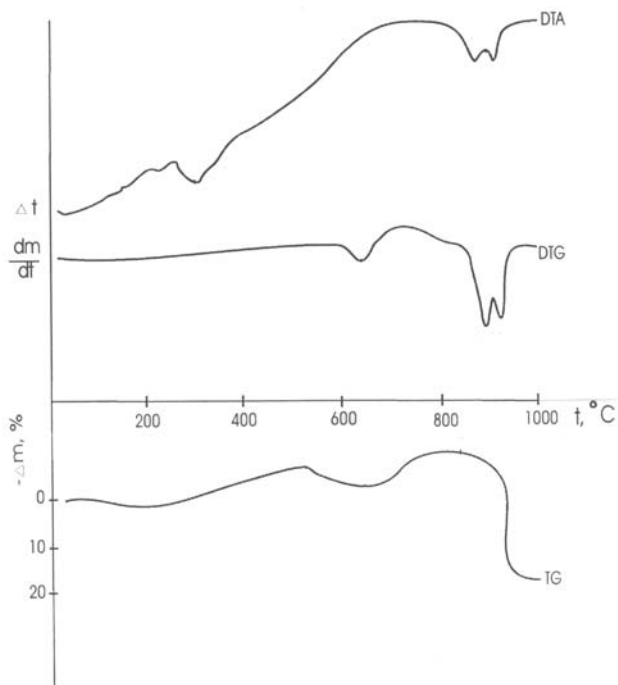


Fig. 3. DTA-TG-DTG analyses of the CoS sample, heating rate 10 °/min

According to the results of thermal analysis following can be concluded: Small endothermic peak occurring on 220°C corresponds to dissociation of Co(OH)S formed after CoS hydration on air which is in agreement with [6]. Further temperature increase results with exothermic peaks accompanied with mass changes on TG curve 815°C and followed by two well-developed endothermic peaks. All of the previously stated, can be presented by following equations:



Part of CoSO₄ is dissociating to Co₃O₄ according:



3.2. Kinetics of oxidation

In the course of experiments, samples of CoS were oxidized and amounts of emitted SO₂ were successively registered. These results are presented in Fig. 4.

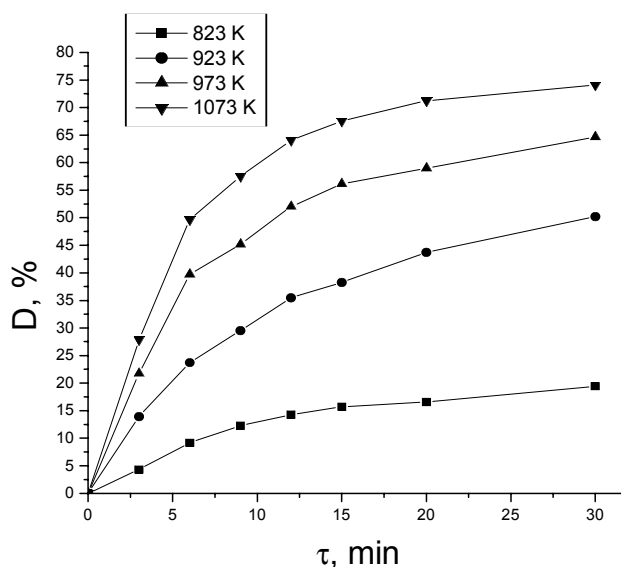


Fig. 4. Amount of sulfur reacted with oxygen during oxidative roasting of CoS sample (D -degree of desulfurization, τ -time)

Linearisation of experimental results, presented in Fig. 4, was tested using nine different kinetic equations, proposed by Sharp [11]. The criteria for accepting an equation as the best for linearisation of the experimental data was the least deviation of experimental curve ($\tau/\tau_{0,5}$) in comparison with curves presenting kinetic equations proposed by Sharp, Fig. 5. Where ($\tau/\tau_{0,5}$) is reduced half time of reaction. This method for selection of kinetic equation for optimal fit of experimental data points was described earlier [13,14].

Using equation $F_1: -\ln(1-\alpha) = k \cdot \tau$ for desulfurization where: α - degree of reaction, t -time, k -rate constant, best linearisation of

experimental data was performed (i.e. minimum standard deviation for all the isotherms), Fig. 6. According to the Sharp's theory, equation F_3 describes reaction with random formation of new phase nuclei and describes kinetic mechanism of reaction [11].

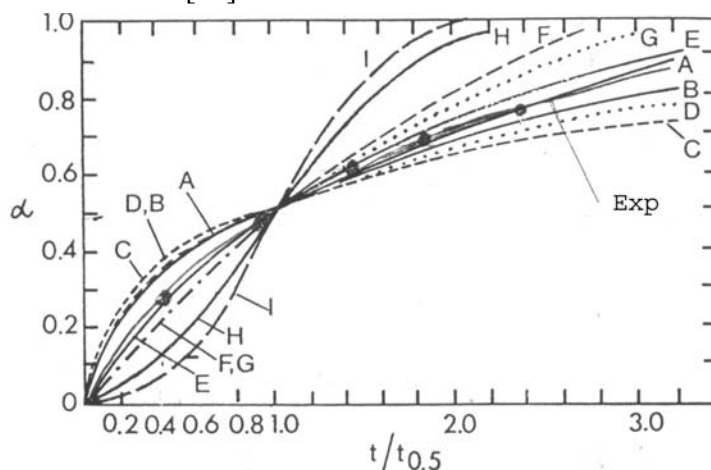


Fig. 5. Comparison of experimental curve with nine kinetic equations proposed by Sharp: A: $D_1(\alpha)$; B: $D_2(\alpha)$; C: $D_3(\alpha)$; D: $D_4(\alpha)$; E: $F_1(\alpha)$; F: $R_2(\alpha)$; G: $R_3(\alpha)$; H: $A_2(\alpha)$; I: $A_3(\alpha)$

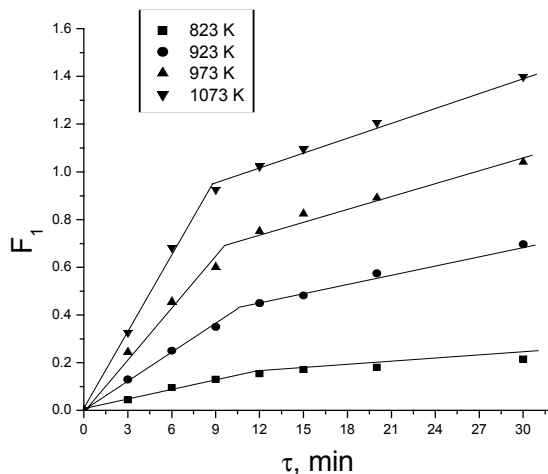


Fig. 6. Linearisation of experimental data points using kinetic equation R_3 for the investigated desulfurization process

From the slopes of the linearized isotherms, rate constants were determined and an Arrhenius diagram, Fig. 7., constructed.

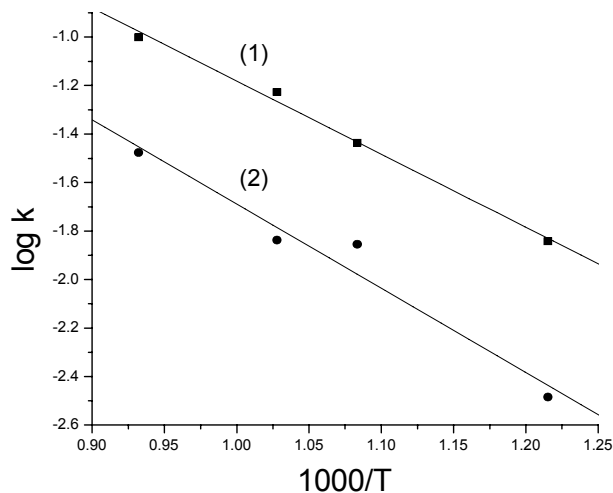


Fig. 7. Arrhenius diagram for the process of CoS oxidative roasting constructed from the slope of sulfur removal during the process

According to the Arrhenius diagrams, activation energy of the process, under isothermal conditions was calculated. The kinetic equation for desulfurization was found to be: $-\ln(1-a) = k \cdot \tau = 68,18 \cdot \exp(-6976/T) \cdot \tau$, with activation energy of 58 kJ/mol for period of oxidation described with line (1) on Arrhenius diagram. After the change of reaction mechanism, line (2) on Arrhenius diagram, kinetic equation was: $-\ln(1-a) = k \cdot \tau = 60,756 \cdot \exp(-7938/T) \cdot \tau$, with activation energy of 66 kJ/mol.

4. Discussion

The two stage model of oxidation presented above could also be concluded by observing TG curve presented in Fig.3. On TG curve there is first increase of weight in temperature range up to 838 K. This increase could be related to CoS oxidation to CoSO₄, which is also indicated by X-ray analysis at 923K

where traces of CoSO_4 are still present in analyzed product of reaction. Further temperature rise leads to weight decrease which can be related to CoSO_4 surface dissociation to CoO until dense oxide layer is formed. Second weight increase is present in temperature interval 923 to 1088 K and could be related to CoO oxidation to Co_3O_4 . This second mass increase could happen after dense oxide layer is formed. In this stage process rate is limited with SO_2 diffusion through this layer. The argument for this statement could be the presence of small amount CoSO_4 in X-Ray obtained even at 1073 K. This constituent is remained in the core of the investigated sample grain while at the grain surface, oxidation of CoO layer to Co_3O_4 is happening.

5. Conclusions

Suggested mechanism of oxidation of CoS at experimental conditions may be summarized as follows: at the beginning, direct oxidation of sulfide proceeds with emission of SO_2 and formation of the porous structure of CoSO_4 . It is accompanied by dissociation of CoSO_4 to CoO . Oxidation moves far into the grain. The product of oxidation, CoO , is oxidized to Co_3O_4 and cobalt sulfate is captured in the grains core. Kinetic parameters calculated for both stages of oxidation process are placing the reaction in the kinetic area.

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