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REACTIONS OF $CoS_{1.023}$ AND Co_3O_4 WITH AIR AND AIR/SO_2 MIXTURES

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Abstract

It was reported in literature, that CoS_{1+y} oxidizes to CoO only, although it appears from Co–S–O predominance phase diagrams, that $CoSO_4$ is stable phase at partial pressures of SO_2 typical for sulfides oxidation. The experiments with $CoS_{1.023}$ oxidation with the air and the air/SO_2 gas mixture described in this paper, reveal that $CoSO_4$ phase is a product of such oxidation. However, the quantity of $CoSO_4$ is only of 1.4% of total cobalt content in the sample oxidized with the air and of 5.6–10.8% for oxidation with the air/SO_2 gas mixture. It is probably due to CoO layer, formed on $CoS_{1.023}$ grain's core, which results in hindering of oxidation after several minutes during the process.

Keywords: cobalt oxide, cobalt sulfate, cobalt sulfide, oxide sulphatizing, sulfide oxidation

Introduction

Equilibria between sulfides, oxides and sulfates are important in metallurgy. Therefore, they are systematically investigated [1–7].

It results from Co–S–O predominance phase diagrams, Fig. 1 [8], that – at typical for metallurgy, similar partial pressures of oxygen and sulfur dioxide – $CoSO_4$ is the only stable phase in the system. Thus, oxidation of sulfides and sulphatizing of oxides should result in sulfate as the final product. The results of sulphatizing of Co_3O_4 at carbon presence [8, 9] or Co_3O_4 without carbon [10] with SO_2 (with no admixed gases) were reported in the literature. Using differential thermal analysis it was found [10] that the mass of the Co_3O_4 sample (without carbon) increased regularly above 673 K up to a maximum of 26.5% at 943 K, then was stable. The mixture of CoO and $CoSO_4$ was the product of this process and the increase of the sample mass was in agreement with the stoichiometry of reaction $Co_3O_4+SO_2=2CoO+CoSO_4$. Sulphatizing of some other metal oxides or their mixtures, e.g. oceanic nodules with oxides of iron, copper, manganese, cobalt and nickel was also investigated. This paper presents some preliminary results of cobalt sulfide, $CoS_{1.023}$, oxidation with the

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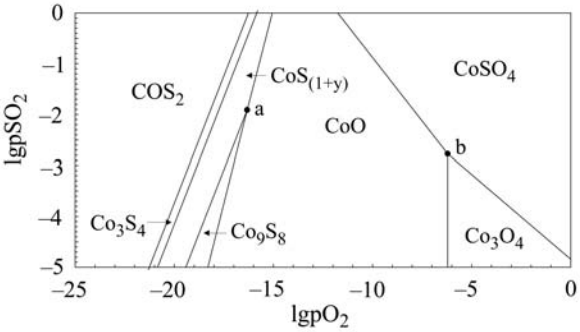

Fig. 1 Co–S–O predominance phase diagram at 883 K. The diagram was calculated by authors of this paper with data from Jacinto *et al.* Ref. [8]

air and its mixture with SO_2, compared with sulphatizing of Co_3O_4 with similar gas mixture (the air $+SO_2$). The question was in efficiency of such processes with respect to cobalt sulfide or oxide transformation to sulfate form.

Cobalt sulfide synthesis and measurements

Synthesis

Cobalt sulfide was prepared from elements according to method described by Asaki *et al*. [11]. Powdered cobalt metal (Merck p.a.) and sublimated sulfur (POCH p.a.) in excess were heated in the quartz ampoule in the vacuum at 0.1 Pa and 520 K for 24 h. Then the ampoule was sealed (closed) and heated to 1420–1450 K. At this temperature the ampoule was kept for 10–20 min then the temperature was decreased to 970 K. The sample was heated at this temperature for the next 5 h and the ampoule was rapidly cooled in water. The surface of the sample was black and its cross-section solid was silver/silver-grey. The cobalt sulfide ingot was crushed into grains which were classified in fractions with specific densities 2.24–2.49 g cm^{-3}. Both fractions – coarse (0.63–0.80 mm) and powder (<0.10 mm) were used in experiments with the air/SO_2 mixture and the intermediate fraction (0.25–0.40 mm) in an experiment with $CoS_{1.023}$ – oxidation with air. Chemical analyses of two samples of synthesized sulfide were performed in the Quality Research Centre Ltd. (Lubin, Poland). Atomic Absorption Spectrometry was used in determination of cobalt while sulfur was analyzed with Inductively Coupled Plasma method. Analyses gave cobalt sulfide stoichiometry of $CoS_{1.019}$ for the first sample and $CoS_{1.026}$ for the second one. So the mean value of $CoS_{1.023}$ was accepted as representative. It is in a good agreement with results of X-ray microanalysis of 0.63–0.80 mm fraction grains (will be published in the next paper). $CoS_{1.023}$ represents non-stechiometry area in the Co–S phase diagram [12].

Measurements

Measurements were carried out with two quartz cells presented in Fig. 2. The cell A was used in experiments with fine fractions, the cell B in experiments with coarse fraction.

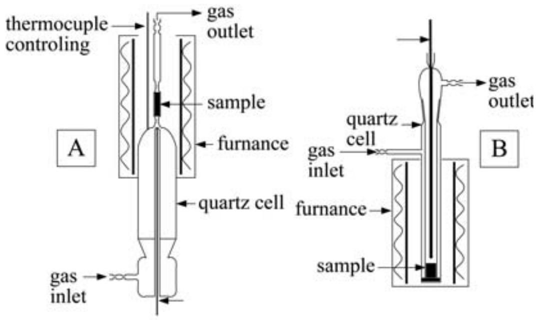

Fig. 2 Measuring cells for investigations of coarse (0.63–0.80 mm) and intermediate (0.25–0.40 mm) fractions of $CoS_{1.023}$ (type A) and fine fractions (<0.10 mm) of $CoS_{1.023}$ and Co_3O_4 (type B)

Reaction gas – the air or mixture of SO_2 with air – was introduced to the main part of the cell A (lower part) or outer part of the cell B (it facilitated to heat up the gas), then penetrated investigated samples (separated from other parts of cells with quartz wool or kaolin fibre) and finally run off at the top of the cells. Gases – compressed air, technical grade argon (Linde Gaz Polska Ltd.) and sulfur dioxide (Messer Polska Ltd.) – were mixed with 3-way glass valves and their flow was controlled with flow-meters RCM 06-3 and ROS-06 (Rotametr Ltd., Poland). The temperature of the furnace/quartz cell arrangement was controlled with the supply/control unit RE31 (Lumel Ltd., Poland) equipped with Pt10%Rh/Pt thermocouple. Iodometric analysis of SO_2 content in reaction gas was performed in experiment of $CoS_{1.023}$ oxidation with the air.

Results

Sulphatizing of Co_3O_4 with the air/SO_2 mixture

Powdered Co_3O_4 (Fluka AG p.a., fraction <0.10 mm) was used in the sulphatizing experiment which was performed in the cell of type B (Fig. 2) at the temperature of 953 K. The air and SO_2 flows were equal to 7.6±0.5 and 4.2±0.4 $dm^3\ h^{-1}$, respectively. The cell with Co_3O_4 was flushed for 10 min with argon before the experiment and dur-

Table 1 Results of sulphatizing and oxidation experiments

Fraction/mm	T/K	Time/min	Mass of the sample/g	% of Co in $CoSO_4$ form
		Sulphatizing of Co_3O_4 with the air/SO_2 mixture		
<0.10	953	150	1.7696	25.5
		Oxidation of $CoS_{1.023}$ with the air/SO_2 mixture		
0.63–0.80	953	603	0.6276	5.6
<0.10	953	682	2.2964	10.8
		Oxidation of $CoS_{1.023}$ with the air		
0.25–0.40	933	323	0.5242	1.4

ing heating to 953 K, and for 15 min after experiment had been completed. The sintered sample of the product of sulphatizing was green-black. It was leached with hot water in order to extract cobalt sulfate. The concentration of cobalt in the water solution after leaching was determined by ASA and on the basis of this analysis it was calculated that 25.5% of cobalt from the oxide form was transformed into sulfate (Table 1).

Oxidation of $CoS_{1.023}$ with the air/SO_2 mixture

Two experiments of cobalt sulfide were performed – one with coarse fraction (0.63–0.80 mm) in the cell of type A and second with fine fraction (<0.10 mm) in the cell of type B (Fig. 2). Both experiments were performed at 953 K at the air and SO_2 flows of 7.6 ± 0.5 and 4.2 ± 0.4 dm^3 h^{-1}, respectively. The cells with cobalt sulfide were flushed with argon before and after the experiments. The product of oxidation of 0.63–0.80 mm fraction was loose and black whereas oxidized <0.10 mm fraction was sintered and – similarly to oxide after sulphatizing process – green-black. Both samples were leached with hot water in order to extract cobalt sulfate and, finally, the degree of cobalt sulfide transformation to sulfate was calculated. Some parameters of the experiments and results of oxidation are presented in Table 1.

Oxidation of $CoS_{1.023}$ with the air

The intermediate fraction 0.25–0.40 mm of $CoS_{1.023}$ was used in this experiment. The fraction was oxidized in the cell of type A at temperature of 933 K for 323 min. SO_2 evolved in reaction of sulfide with passing through the bed gas was absorbed in portions of iodine solution containing a known quantity of iodine. The time for decolorizing of the solution enabled precision calculations of the SO_2 evolution rate (Fig. 3). The experiment was finished when no further SO_2 evolution had been observed. Oxidized sulfide grains were analyzed with scanning microscopy (JSM 5800L microscope) before and after the oxidation process. Comparison of these two images is presented in Fig. 4. Before oxidation (Fig. 4a) the sample consisted of dense grains with sharp edges, with only single grains partially porous. It was detected with X-ray microanalysis that small amounts of oxygen were adsorbed on the surface of dense grains (due to handling in the air before analysis). The concentration of oxygen on the surface

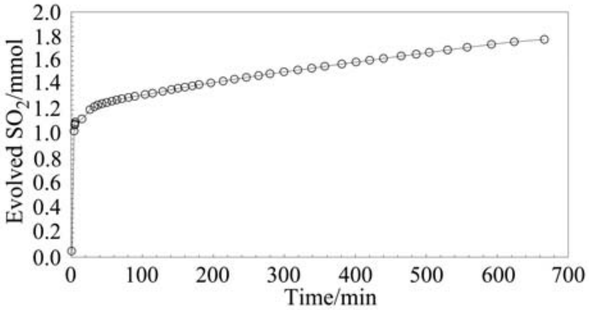

Fig. 3 SO_2 evolution during oxidation of 0.25–0.40 mm fraction of $CoS_{1.023}$ with the air at 933 K

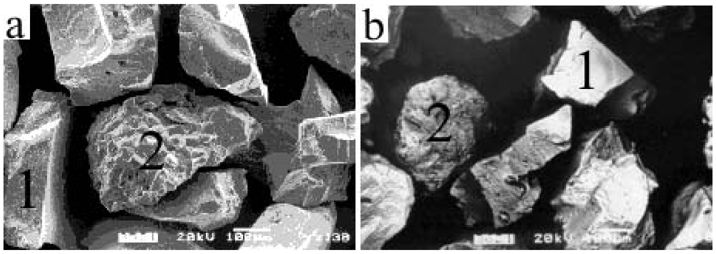

Fig. 4 Microscopic analysis of 0.25–0.40 mm fraction of $CoS_{1.023}$ a – before and b – after oxidation with the air at 933 K. 1 – dense grains, 2 – porous grains (description in the text)

of observed porous grain was rather high, which suggested its partial oxidation. After oxidation (Fig. 4b) there still were numerous dense grains with well formed sharp edges and less numerous porous or partially porous grains. There was no sulfur detected on surface of dense grains and the molar proportion between oxygen and sulfur was equal to 1.5:1, what indicated presence of Co_3O_4 as the only form of cobalt oxide. On the other hand, the sulfur was still present on the surface of porous grains. We believe that it was cobalt sulfate, $CoSO_4$.

Generally, transformation of cobalt sulfide, calculated on the basis of SO_2 emission, was rather high – as much as 85.2% of the sulfur originally in the form of $CoS_{1.023}$ was oxidized to SO_2. At the same time only 1.4% of cobalt was extracted to the water solution (in the form of cobalt sulfate).

Discussion

It was suggested in the [11] that cobalt sulfide oxidizes in air to cobalt oxide CoO and the mechanism of oxidation consists of cobalt diffusion from sulfide followed by its oxidation with no (or almost no) SO_2 emission. We believe that the formation of a dense layer of cobalt oxide on the sulfide surface (more or less with cobalt diffusion) is responsible for the incomplete reaction of cobalt sulfide and the specific shape, presented in Fig. 3 curve of SO_2 evolution. So, we believe that the cores of dense grains in Fig. 4b are still unreacted sulfide surrounded by oxide layers. Although we detected Co_3O_4 oxide on the grain's surface, it is very probable that CoO oxide still existed inside the grains, directly on the sulfide cores. This model is in agreement with Co–S–O predominance phase diagram (Fig. 1), because CoS_{1+y} oxidation must proceed to cobalt(II) oxide, CoO, followed by sulfation to $CoSO_4$ at higher pressures of SO_2 (this situation should take place inside cobalt sulfide grains).

But we also detected grains (porous) with sulfur directly on their surface, and registered small amounts of cobalt which were dissolved in water (cobalt sulfate is the only form soluble in water in this experiment). Therefore additional reactions should be considered for the cobalt sulfide oxidation process. We assumed that it should be sulphatizing process of cobalt oxides – CoO or Co_3O_4 (if oxidation of CoO to Co_3O_4 is more favourable than direct sulphatizing of CoO) with evolved during oxidation of sulfide SO_2. To verify this assumption we performed two experiments with oxidation of $CoS_{1.023}$ (original sulfide) with a mixture of air and SO_2 – with coarse and fine fractions of sulfide. And we found that degree of transformation of cobalt sulfide to the sulfate form is significantly higher (Table 1) in the case of gas mixture air/SO_2 than in air only. Moreover, transformation of the fine fraction is twice as high, which is additional evidence that sulphatizing depends on the extent of contact surface between gas with high SO_2 pressure and cobalt oxide. We repeated the same experiment with fine fraction of Co_3O_4 and we found that the degree of transformation of cobalt increased more than twice. We think that it reflects the probability of higher reactivity of Co_3O_4 (affinity to SO_2) in comparison to CoO. But this supposition needs more careful investigations.

Therefore, we concluded that:

- $CoO_{1.023}$ oxidizes in air to cobalt oxides (Co_3O_4 on the grain's surface and CoO inside) admixed with small amounts of cobalt sulfate.
- Oxidation proceeds only during the initial period of several min accompanied with high emission of SO_2 then almost completely decays due to the formation of a dense cobalt oxide (CoO) layer on sulfide core.
- Enrichment of the oxidizing gas with SO_2 significantly increases amount of cobalt sulfate formed.
- Sulphatizing of cobalt oxide Co_3O_4 is significantly more efficient than oxidation with the same gas mixture of cobalt sulfide $CoS_{1.023}$, probably due to the formation of the CoO layer on the sulfide core hindering its oxidation.

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