

Cadmium sulphide oxidation[☆]

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Abstract

Systematic investigations have been carried out on the oxidation of CdS of semiconductor purity using both DTA, and TGA, as well as chemical, mineralogical, phase X-ray analysis and scanning electron microscopy (SEM). The paper presents a three-dimensional phase diagram for the Cd–S–O system of partial pressure of SO₂ and O₂ against *T* in the temperature interval 600–1000 °C, from thermodynamic of the system.

DTA, TGA and X-ray analysis of the product obtained from roasting are compared with the thermodynamic predictions from the three-dimensional diagram.

Plates of hexagonal monocrystal CdS were very porous and on oxidizing a mechanically weak layer of CdO was obtained. The CdO crystals grow both towards the core of the particle and outwards in the direction of the gas phase in the air environment through condensation of the vapour. The oxidation processes take place in a kinetically controlled regime and oxidation does not follow the classical model of the continuously shrinking unreacted core. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cadmium sulphide; Oxidation; Thermodynamic; DTA; TGA; Powder X-ray analysis; SEM

1. Introduction

Oxidation of metal sulphides is a complicated exothermal heterogeneous process, influenced by chemical, crystal chemical, adsorption, mass-exchange, heat-exchange and other kinds of processes. The progress of the chemical reactions is connected with changes in the reacting surface and its accessibility in the course of time.

In previous research, experiments have been made with synthetic pulverous CdS in a static atmosphere [1–5]. The evaporation and thermal dissociation of CdS were not discussed [6] and the conditions of the experiments did not allow the complete mechanism of the oxidation process to be elucidated but it was apparent that diffusion and secondary reactions were dominant. The present paper aims at clarifying the behaviour of a particle of CdS when thermally treated, in the way metal sulphide concentrates are roasted.

The study of the CdS oxidation process are of interest both for the processing of zinc and poly-metallic sulphide concentrates, and for producing heterogeneous semiconductor from the transition of CdS–CdO.

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2. Experimental

Systematic investigations have been made of the oxidation of pulverised and single crystals of CdS of semiconductor purity (concentration of carriers 10^{14}). The CdS sample had a hexagonal unit cell with lattice parameters $a = 4.1348 \text{ \AA}$ and $c = 6.7490 \text{ \AA}$. Plates of $2 \text{ mm} \times 5 \text{ mm} \times 0.5 \text{ mm}$ were split-off from sample.

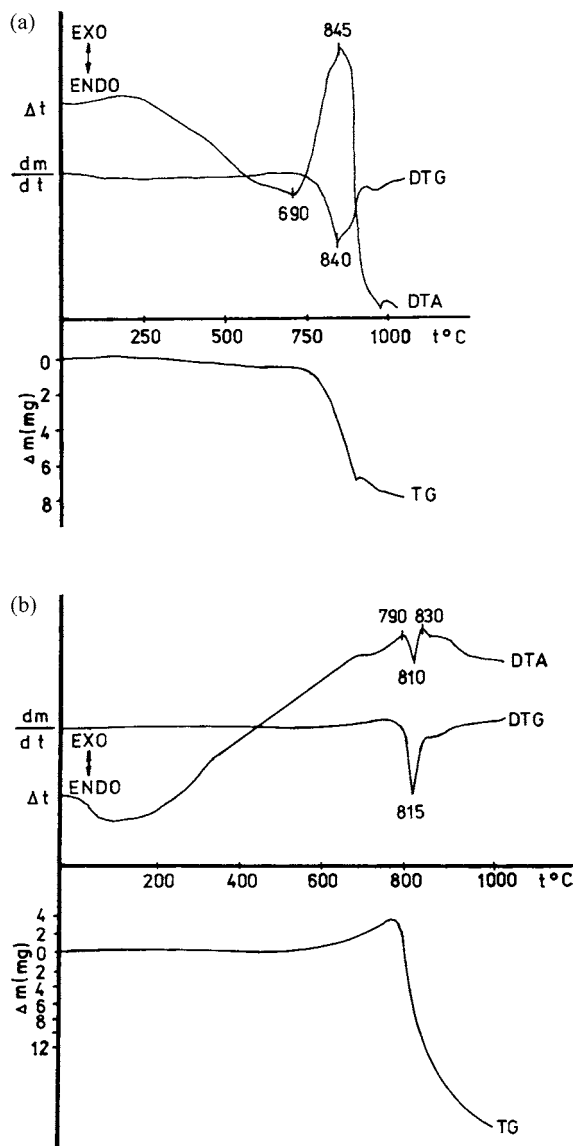


Fig. 1. Derivatograms of CdS in air atmosphere: (a) Netzsch STA 429, mass of the sample, 50 mg, following air; (b) Derivatograph-Q, mass of the sample, 250 mg, static air atmosphere.

Thermogravimetric analysis was carried out in two laboratories using different equipment: Netzsch STA 429 (Fig. 1a) and a Derivatograph-Q manufactured by the Hungarian firm MOM (Fig. 1b). The working conditions were for the STA 50 mg; $10^\circ\text{C min}^{-1}$; 100 l h^{-1} flowing air; DTA: 0.1 mV; TG: 25 mg, DTG: 0.2 mV; fraction $< 0.063 \text{ mm}$ and for the Derivatograph-Q 250 mg; $10^\circ\text{C min}^{-1}$; static air atmosphere; DTA: 1 mV; DTG: 2.5 mV; TG: 100 mg, fraction $< 0.063 \text{ mm}$. The analyses were made in platinum crucibles using Al_2O_3 as the reference material.

Synthetic pulverised CdS was roasted under isothermal conditions in a roasting furnace under laboratory conditions at the following temperatures: 500, 600, 800, 1000°C . The mass of the samples was 200 mg. The oxidant was air and the heating time 1 h. The calcine produced was subjected to powder X-ray diffraction analysis using Philips Diffractometer with a $\text{K}\alpha$ radiation. SEM analyses were carried out on oxidised CdS plates split from the sample using a Super Probe 733.

3. Results and discussion

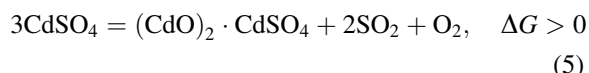
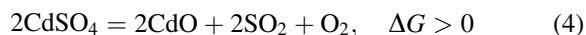
3.1. Thermodynamic analysis

Two methods of the thermodynamic study were used:

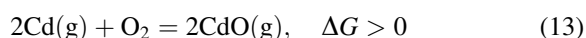
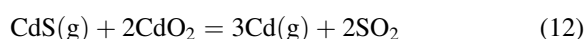
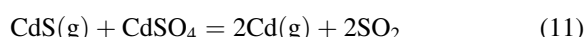
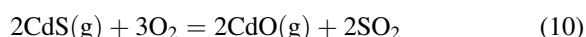
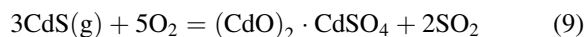
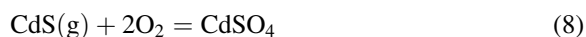
1. By the calculated ΔG and K [7].
2. By drawing a three-dimensional diagram of partial pressures [8–16] of SO_2 and O_2 against T for the Cd–S–O system.

Experiment were carried out in the temperature range $600\text{--}1000^\circ\text{C}$. The O_2 content in the gas phase was in the range of 1–21% and SO_2 content within the range 1–14%, thus encompassing the practical conditions of roasting [17]. HSC software was used to determine the thermodynamic parameters, ΔG and K for each reaction. In the temperature interval investigated, the possible chemical reactions that could take place to some extent or another, depending on conditions, are as follows:





At temperatures higher than 800 °C:



The thermodynamic characteristics of the most probable phase equilibriums ($\Delta G < 0$) at 600, 700, 800, 900 and 1000 °C and 1 mol CdS are presented in Tables 1 and 2.

Fig. 2 shows the three-dimensional diagram of the partial pressures of SO_2 and O_2 against T for the Cd–S–O system for the temperature interval 600–1000 °C which is of interest for the processing of metal sulphide concentrates.

The stability of the phases changes with increase in temperature:



[·]^{*}-phase, stable only at certain temperature and gas phase composition.

3.2. Thermogravimetric analysis

In [1,2,14,17] two mechanism for CdS oxidation are presented based on an oxide and sulfate. Examples are given in [5] to support the fact that CdS oxidation follows one of these mechanisms depending on the source and structure of CdS, and the experimental conditions.

Results from the thermogravimetric and derivatographic analyses are shown in Fig. 1a and b. It should

Table 1

Gibbs free energy change and the equilibrium constants for the most probable solid phase chemical equilibrium in the Cd–S–O system in the temperature interval 600–1000 °C

| T (°C) | Reaction (1) | | Reaction (2) | | Reaction (3) | | Reaction (6) | |
|----------|------------------------------------|----------------------|------------------------------------|-----------------------|------------------------------------|----------------------|------------------------------------|----------------------|
| | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K |
| 600 | -475.9 | 2.9×10^{28} | -393.3 | 3.9×10^{70} | -343.7 | 1.3×10^{41} | 129.8 | 1.7×10^{-8} |
| 700 | -441.0 | 4.7×10^{23} | -378.2 | 8.1×10^{60} | -336.2 | 1.2×10^{36} | 88.8 | 1.7×10^{-5} |
| 800 | -406.5 | 6.1×10^{19} | -363.3 | 1.1×10^{53} | -328.7 | 1.0×10^{32} | 48.3 | 4.4×10^{-3} |
| 900 | -373.1 | 4.1×10^{16} | -348.4 | -3.4×10^{46} | -321.1 | 4.0×10^{28} | 9.2 | 3.9×10^{-1} |
| 1000 | -347.6 | 9.4×10^{13} | -333.4 | 1.1×10^{41} | -313.6 | 5.4×10^{25} | -28.9 | 1.5×10^1 |

Table 2

Changes in the Gibbs free energy and the equilibrium constant of the most probable chemical equilibrium in the Cd–S–O system for temperatures higher than the sublimation temperature of CdS

| T (°C) | Reaction (8) | | Reaction (9) | | Reaction (10) | | Reaction (11) | | Reaction (12) | | Reaction (14) | |
|----------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|----------------------|------------------------------------|-------------------|------------------------------------|----------------------|------------------------------------|-------------------|
| | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K | ΔG (kJ mol ⁻¹) | K |
| 800 | -558.0 | 1.4×10^{27} | -514.7 | 1.5×10^{75} | -324.5 | 3.9×10^{31} | -109.8 | 2.2×10^5 | -325.6 | 1.5×10^{17} | -34.4 | 4.7×10^1 |
| 900 | -508.6 | 4.4×10^{22} | -483.8 | 4.3×10^{64} | -317.2 | 1.8×10^{28} | -151.9 | 5.8×10^6 | -356.4 | 7.4×10^{15} | -23.1 | 1.1×10^1 |
| 1000 | -406.2 | 7.6×10^{18} | -453.1 | 5.9×10^{55} | -309.9 | 2.7×10^{25} | -193.1 | 8.4×10^7 | -360.3 | 6.1×10^{14} | -12.4 | 3.2 |

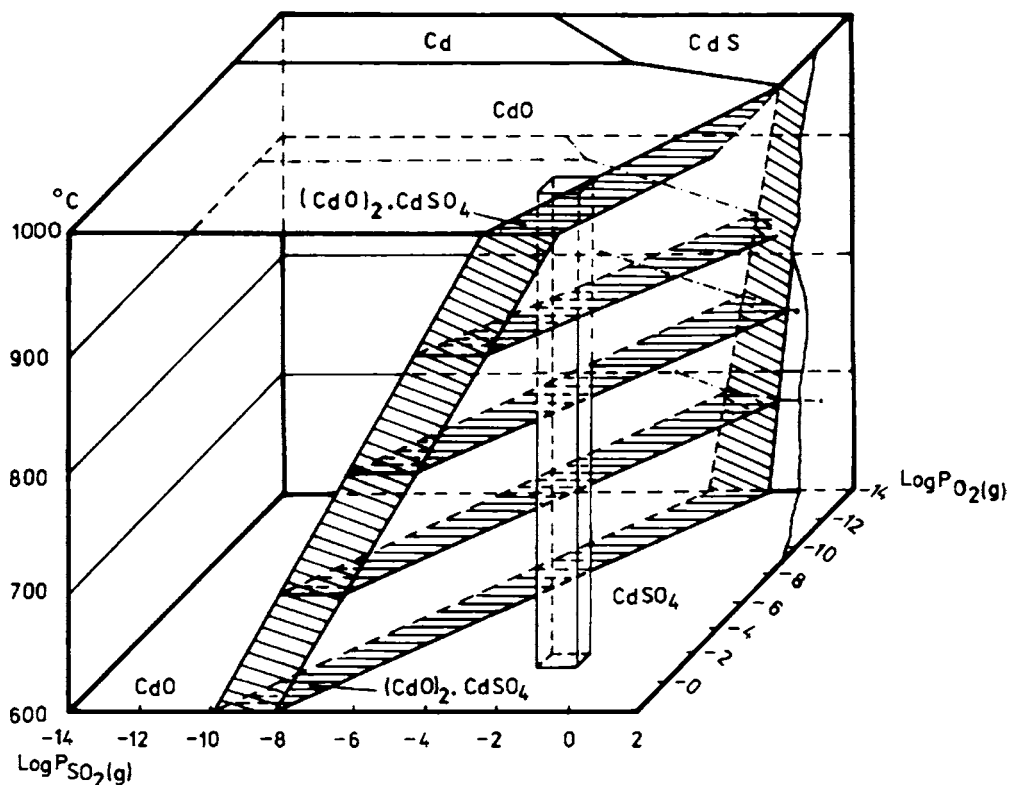


Fig. 2. Three-dimensional phase diagram of partial pressures of the Cd–S–O system. Co-ordinates $\lg P_{\text{SO}_2}$ – $\lg P_{\text{O}_2}$ – T . Temperature interval 600–1000 °C.

be pointed out that there is a difference between the derivatograms. The sample with the smaller mass in Fig. 1a has a maximum in the DTA and DTG curves at about 840 °C. The sample mass decreases in the interval from 680 to 1000 °C. The sample mass loss is ~16%, while, theoretically, if the whole quantity of CdS turns into CdO Δm would be ~11%. The probable reason for this is the sublimation of CdS, as well as oxidation. Under these conditions no mass gain was registered as a result of sulphate formation and no endotherm characteristic of the dissociation of the sulphate was observed either.

The derivatogram of the sample with five-fold increase in mass (see Fig. 1b) in static air atmosphere showed some gain in mass in the temperature region 500–780 °C. The process was exothermic and was Δm about 2%.

Most probably sulphate was obtained which at 780 °C began to react with the unreacted sulphide. A maximum in the endothermic was observed at

820 °C and at the same time the mass of the sample continued to decrease (at 1000 °C Δm was ~8.5%). This could be explained by the reaction between the sulphate and sulphide and evaporation of CdS. The sublimation temperature of CdS is 796 °C.

In addition to these thermogravimetric study, the thermal treatment of CdS was carried out, with time, in flowing 99.99% nitrogen and air, at a heating rate of 10 °C min⁻¹ and a constant temperature of 750 °C (Fig. 3). The sublimation and dissociation of CdS which resulted in the emission of sulphur vapour have been confirmed by others [6,7]. In flowing air, the processes occur at the lower temperatures with the emission of considerably larger quantities of sulphur.

It is possible that the exothermic process resulted in local overheating of CdS which resulted in evaporation and dissociation of larger quantities of CdS, and therefore leads to a higher extent of desulfurisation. But a parallel “primary” oxidation of the solid state

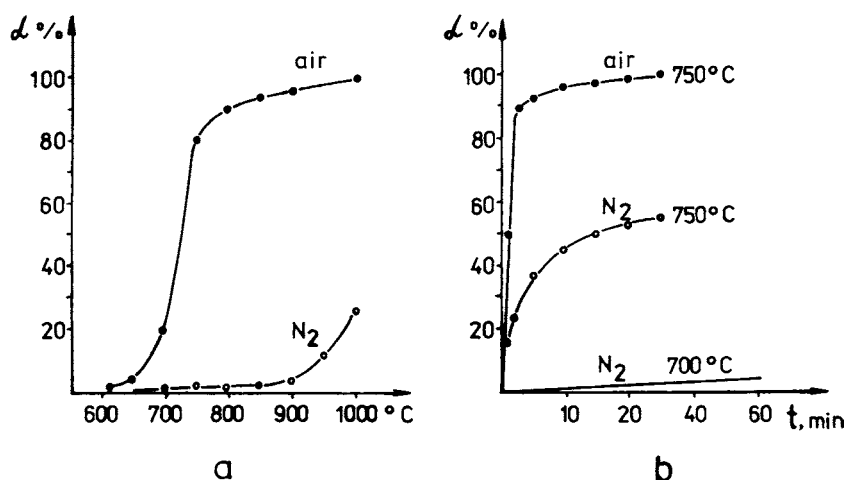


Fig. 3. Changes in the extent of desulphurisation (α) of CdS: (a) when heated at a constant heating rate of $10^{\circ}\text{C min}^{-1}$; (b) dependence on the time (t).

CdS with a “secondary” oxidation of the CdS or Cd vapours obtained in sublimation and dissociation of CdS, may also be possible. According to Tatzenko [3] formation of Cd is possible as a result of an interaction between the sulphide and oxide.

Schultze et al. [18] have obtained very interesting results from the oxidation of different modifications of ZnS: sphalerite and wurtzite. Wurtzite, the high temperature hexagonal modification, is oxidised directly to ZnO without any detectable side reactions or intermediate products. Sphalerite, the low temperature cubical modification of ZnS starts to oxidise at lower temperature. ZnSO_4 and $\text{Zn}_3\text{O}(\text{SO}_4)_2$ are formed as intermediates in side reactions but yielded ZnO finally. The high temperature hexagonal monocrystalline CdS is oxidised directly to CdO.

In the oxidation of synthetic powdered CdS (obtained by precipitation) under the conditions used above, i.e. a large sample and absence of air flow, intermediate sulphate products are probably produced as a result of oxygen deficiency and the large mass of CdS in the crucible. Under those conditions the composition of the gas phase changes.

3.3. X-ray analysis

The initial formation of sulfate begins at a temperature lower than 500 $^{\circ}\text{C}$; at 500 $^{\circ}\text{C}$ it is insignificant, while in the calcine, obtained after the oxidation

of the sample at 600 $^{\circ}\text{C}$, CdSO_4 is the main component present (Fig. 4).

The process of CdS dissociation, under isothermal conditions, most probably begins in the temperature interval 600–800 $^{\circ}\text{C}$. At 800 $^{\circ}\text{C}$, an intermediate product is detected which is $(\text{CdO})_2\cdot\text{CdSO}_4$. At 1000 $^{\circ}\text{C}$ the quantity of CdO is greatest but the dissociation of cadmium sulphate is not completed.

Most of the thermodynamic predictions were confirmed by the results obtained from the DTA–TGA–DTG and X-ray analyses. However, there are some differences in the temperature range 800–900 $^{\circ}\text{C}$ in that the transition from CdS– CdSO_4 –CdO tend in general to take place at comparatively lower temperatures under normal roasting conditions than those predicted by the thermodynamic analysis. The dissociation of CdSO_4 to CdO is quite intensive at $T > 800^{\circ}\text{C}$, while the thermodynamic analysis predicts that the CdO phase at $T > 950^{\circ}\text{C}$ is quite stable. These differences are most probably due to the complicated nature of the heterogeneous processes which is affected by chemical, adsorption, mass–heat-exchange processes, etc. The considerable degree of CdS sublimation should also be taken into consideration.

3.4. Scanning electron microscopy study

SEM analysis showed that the oxidation processes begin on the surface of the CdS plates at temperatures

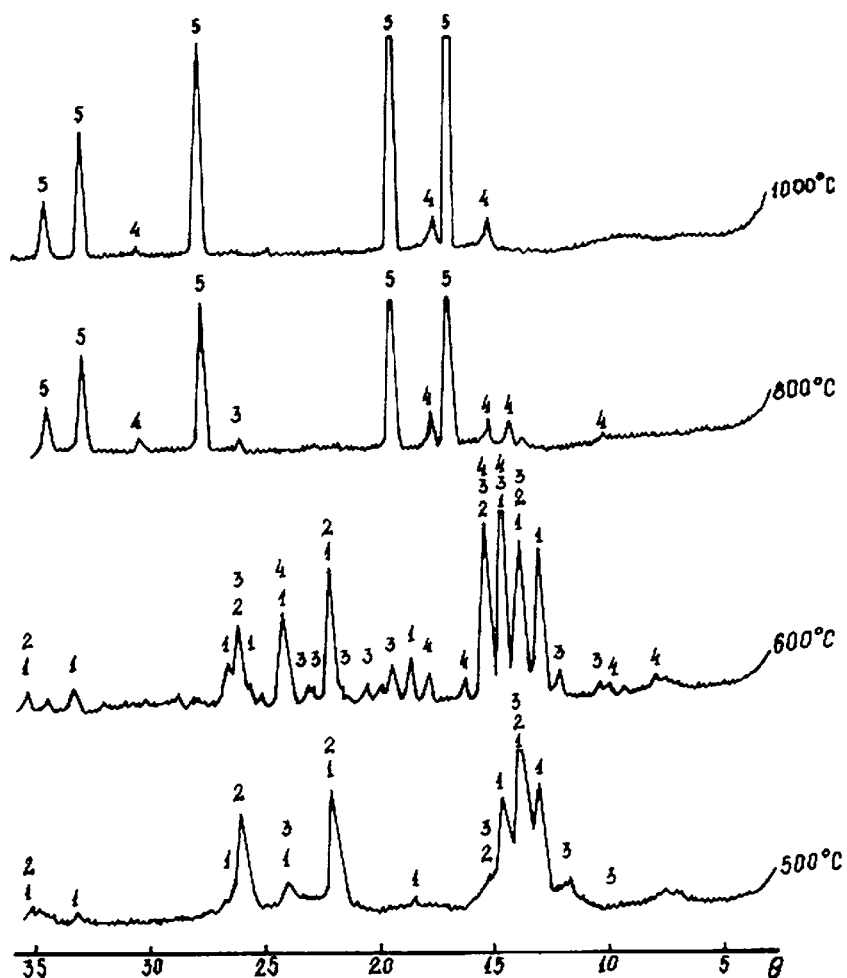


Fig. 4. X-ray diagrams of synthetic powdered CdS, oxidised at: 500, 600, 800, and 1000 °C. (1) α -CdS; (2) β -CdS; (3) CdSO₄; (4) (CdO)₂·CdSO₄; (5) CdO.

comparatively lower than determined by DTA. The new phase appeared in the active centres (at defects) of the sulphide surface and then grew as a result account of the gas phase (Fig. 5).

The crystal oxide crust does not completely cover the surface of the CdS plate and is very porous. At higher oxidation temperatures (750 °C for example), after reaching a certain critical thickness in the course of time, the oxide layer mechanically splits-off from the unreacted sulphide core. Thus, a fresh sulphide surface is exposed to oxidation.

X-ray diffraction analysis proves that the crust is composed of CdO alone. The crystal nuclei reach considerable sizes: up to 100 μm cube-shaped crystals

or a combination of a cube and a pyramidal cube, or sometimes of a cube and a rhombododecahedron and octahedron. Quite often twin crystals are observed.

A possible explanation for the considerable porosity of the oxide crust may be the smaller molar volume of the product of the reaction. The difference between the molar volumes (\AA^3) of CdS and CdO is, using the data from [19]:

$$\Delta V = 49.9616 - 25.8780 = 24.0836$$

or

$$\frac{\Delta V}{V_{\text{CdS}}} \times 100 = \frac{24.0836}{49.9616} \times 100 = 48.2\%$$

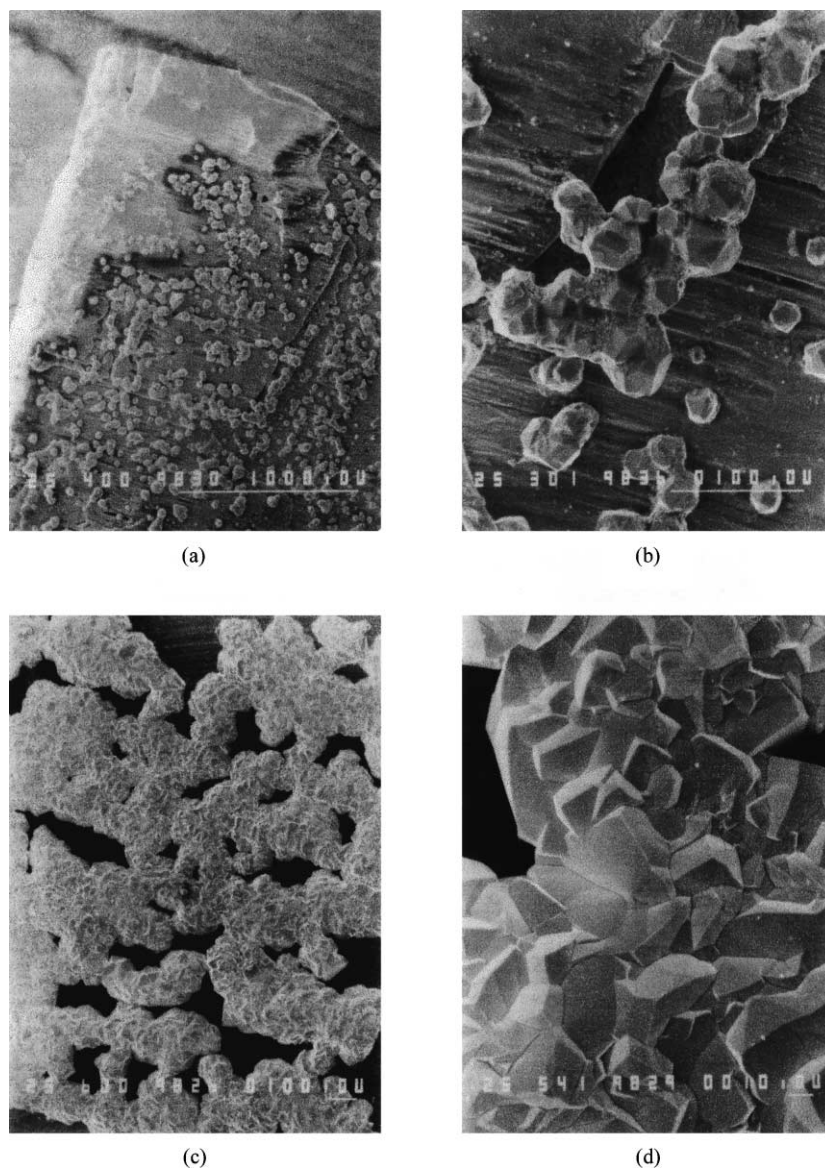


Fig. 5. Electron micrographs of CdS plates oxidised at 750 °C for 5 min: (a) 40 \times ; (b) 300 \times and for 20 min: only oxide crust: (c) 60 \times ; (d) 540 \times .

The CdO obtained from the oxidation of CdS has larger crystallographic unit cell and is more porous, compared to the ZnO [20] obtained from the oxidation of ZnS, for which ($\Delta V/V_{\text{ZnS}}$) is approximately 40.2% [19]. The oxide crust is mechanically weaker and there is no joint between the oxide crust and the unoxidised sulphide core. The adhesion is very weak. It is possible that the high vapour pressure over the base CdS also

has an effect [6]. The process continues both inwards—toward the centre of the particle, and outwards. The CdO crystals grow also in the direction of the gas phase in the air environment through condensation of the vapours (Fig. 6).

In case of fast growth, anisometric, elongated along their triple crystallographic axis, crystals of CdO are formed. These are cubes or octahedrons. At higher

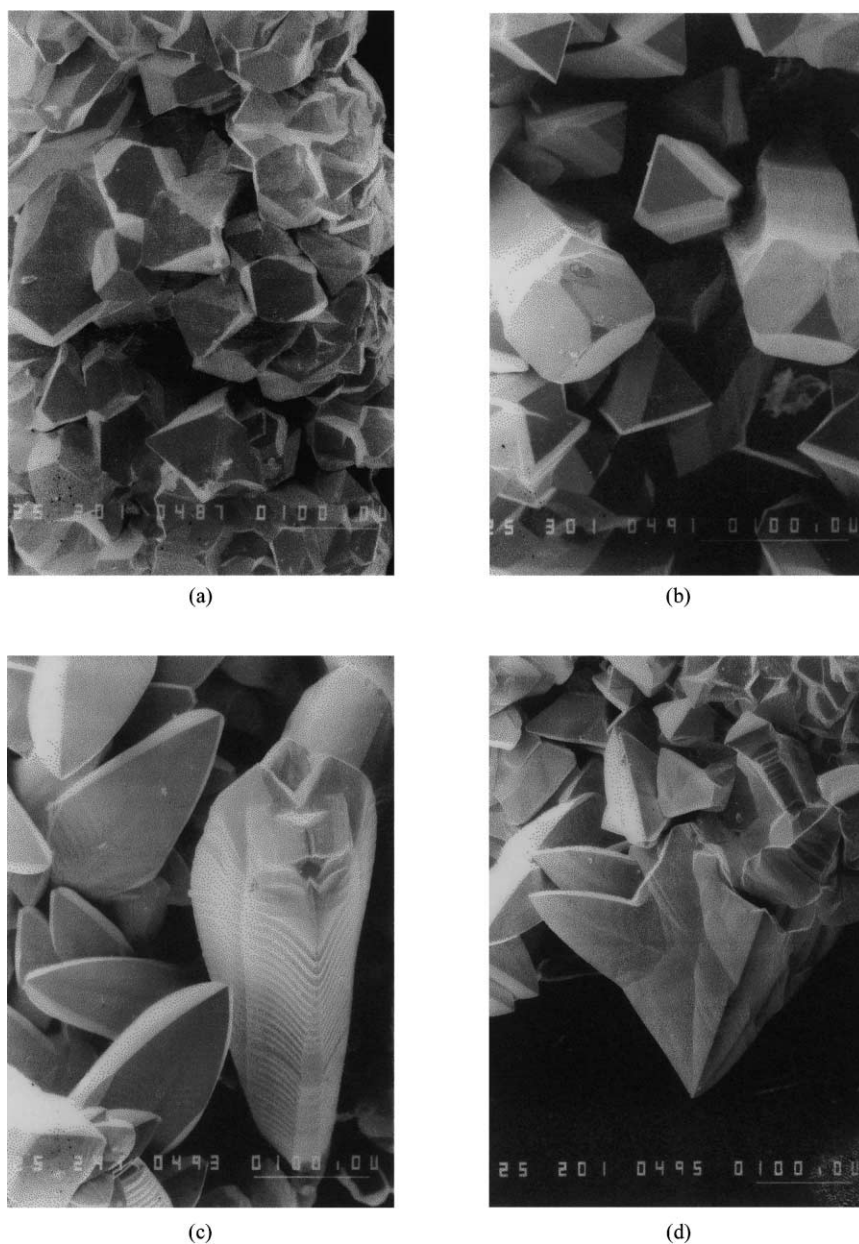


Fig. 6. Electron micrographs of the surfaces of CdS plates oxidised at 600 °C for 2 h: (a) 200 \times and 3 h; (b) 300 \times ; at 750 °C for 0.5 h; (c) 240 \times and 0.75 h; (d) 200 \times .

temperatures (for example 750 °C) the crystals grow faster and their shape suggests that they have grown points to the greater part in the direction of the gas phase. The side walls of the crystals are covered with gilled sculptures resulting from periodic morphological misalliance. The electron microscope analyses also

confirm the large influence of sublimation and dissociation of CdS on its oxidation.

The mechanism of CdS oxidation is somewhat different from that proposed by Tatzenko [3], Yazawa [7] and Lakernik and Pahomova [1]. It is far more complicated involving a topochemical process which

partially follows (at the beginning) a continuously shrinking unreactive core in combination with crystal growth through oxidation of metal cadmium in a gas phase. It is obtained either through reaction between a sulphate and a sulphide (at low temperatures and favourable P_{SO_2} and P_{O_2} [21] or as a result of dissociation of the sublimated CdS (at high temperatures). A very unstable and porous oxide crust is formed which does not obstruct the diffusion of the gaseous reagent (O_2). The crust easily breaks-off from the core and exposes a new reactive surface. This is why under the conditions of a fluid bed furnace the process takes place in a kinetically controlled regime.

4. Conclusion

CdS oxidation is a complicated heterogeneous exothermic process which is affected by a number of complicated processes involving reaction kinetics, crystal chemistry, adsorption, mass-exchange, heat-exchange and other. When roasting sulphide concentrates in the oxidation of CdS, a very porous and mechanically weak CdO crust is obtained. The processes takes place in a kinetically controlled regime. Oxidation does not follow the classical model of the continuously shrinking unreacted core.

Acknowledgements

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