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KINETICS AND MECHANISM OF THE OXIDATION OF MOLYBDENUM SULPHIDE

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Abstract

This paper reports on the results attained in the determination of the mechanism of oxidation of molybdenum sulphide under non-isothermal conditions in an air atmosphere. The mechanism of the process was determined by simultaneous DTA-TG-DTG, and the kinetic parameters of the reactions involved were obtained according to the methods of Kissinger and Ozawa.

Keywords: kinetics, molybdenum sulphide, oxidation

Introduction

The oxidation of molybdenum sulphide has been studied mostly by thermal analysis methods, and different results are given in the literature [1–4].

The oxidizing roast process has been carried out in the temperature range between 673–873 K in oxygen or air atmosphere [1–3]. Shigegaki *et al.* [4] have described exothermic effects in the DTA curve in the course of the oxidation of nonstoichiometric Mo_2S_3: the first at 698 K, the second at 720 K, the third at 776 K, and the fourth at 877 K. These transformations have been interpreted in different ways [5, 6], but without exact details, thus indicating that the mechanism of the process has not been defined adequately.

This paper presents oxidation of molybdenum sulphide – MoS_3 the results obtained by a comparative examination of the process by means of DTA, TG and DTG methods in an air atmosphere, at different heating rates. Based on the results obtained, the kinetic parameters of the process were determined.

Experimental

The molybdenum sulphide – MoS_3 used in the investigations was synthesized in the laboratory of The Institute for Inorganic Chemistry and Metallurgy of Rare

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Metals in Wroclaw (Poland). A derivatograph (MOM, Budapest, Hungary) was used for the thermal examinations.

Results and discussion

The sulphur-oxygen potential diagram for the Mo–S–O system at 1073 K is presented in Fig. 1. Isobaric conditions for SO_2 are presented by inclined, straight lines. A reasonable relation process can be predicted in concentration with practice. Roasting with air may be approximated by following the isobars corresponding to p_{SO_2} values of 10^4 and 10^5 Pa. Thus, according to Fig. 1, the oxidation sequence with increasing oxygen potential is:

$$MoS_3 \xrightarrow{(1)} MoS_2 \xrightarrow{(2)} MoO_2 \xrightarrow{(3)} MoO_3$$

Figure 2 presents the results of a simultaneous DTA-TG-DTG analysis of MoS_3, obtained at a heating rate of 10°C min^{-1} in an air atmosphere. The results indicate that the process of oxidation of molybdenum sulphide involves four steps before the final product, MoO_3, is obtained.

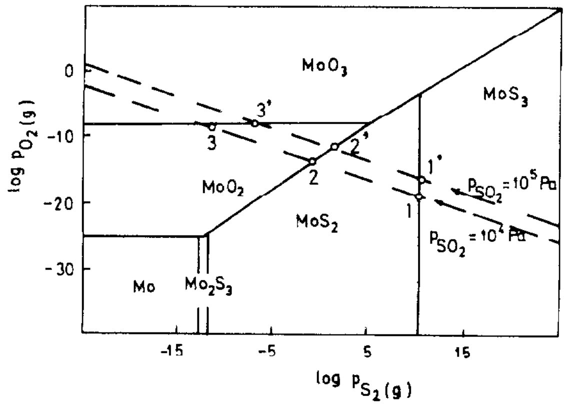

Fig. 1 Sulphur-oxygen potential diagram for the Mo–S–O system at 973 K

From the results presented (Fig. 2), as well as from the results obtained at different heating rates within the range 2.5–20°C min^{-1}, the following processes were determined:

$$MoS_{3(s)}+O_{2(g)} \xrightarrow{(600-550\ K)} MoS_{2(s)}+SO_{2(g)} \tag{1}$$

$$MoS_{2(s)}+3O_{2(g)} \xrightarrow{(710-730\ K)} MoO_{2(s)}+2SO_{2(g)} \tag{2}$$

$$MoO_{2(s)}+0.5O_{2(g)} \xrightarrow{(850-950\ K)} MoO_{3(s)} \tag{3}$$

$$MoO_{3(s)} \xrightarrow{(950-1030\ K)} MoO_{3(g)} \tag{4}$$

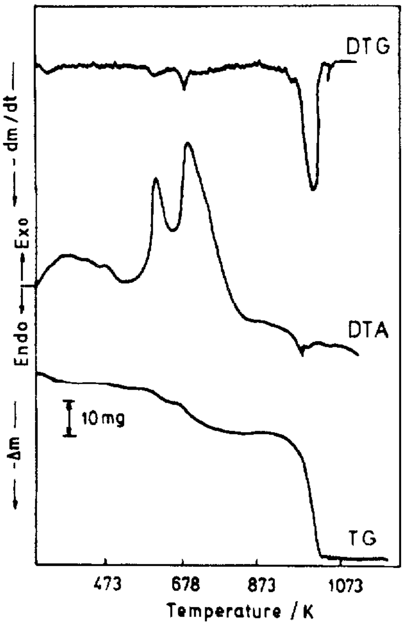

Fig. 2 DTA-TG-DTG analysis of molybdenum sulphide at a heating rate of 10°C $\min^{-1}$ in an air atmosphere

Owing to the nature of the processes considered in Eqs (1–4) and to the form of the thermoanalytical curves obtained (DTA-TG-DTG) the authors decided to determine the kinetic parameters of the processes using the Kissinger [7] and the Ozawa [8] methods, which require certain DTA examinations at different heating rates. The results obtained in DTA examinations at heating rates of 2.5–20°C $\min^{-1}$ are presented in Fig. 3.

The results in Fig. 3 were processed according to the method developed by Kissinger and Ozawa or using [9]:

a) Kissinger

$$\ln(\Phi/T_m^2) = C - E/RT_m \tag{5}$$

b) Ozawa

$$\ln\Phi = C_1 - E/RT_m \tag{6}$$

where: Φ is the heating rate, T_m the maximum in the DTA peak, E the activation energy, R the universal gas constant and C and C_1 are integration constants.

The graphical representation of the dependences $\ln(\Phi/T_m^2)=f(1/T_m)$ and $\ln\Phi=f(1/T_m)$ for the processes defined in Eqs (1)–(4) is presented in Fig. 4 from which the values of the activation energy E and integration constants C and C_1 can be determined. The results obtained are listed in Table 1.

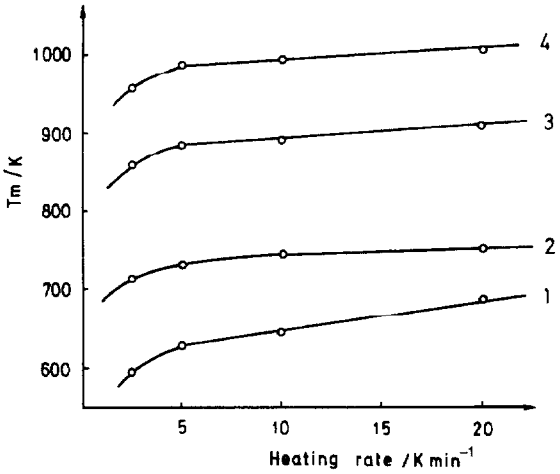

Fig. 3 Dependence of T_m on the heating rate for the processes described by Eqs (1)–(4) during the oxidation of molybdenum sulphide

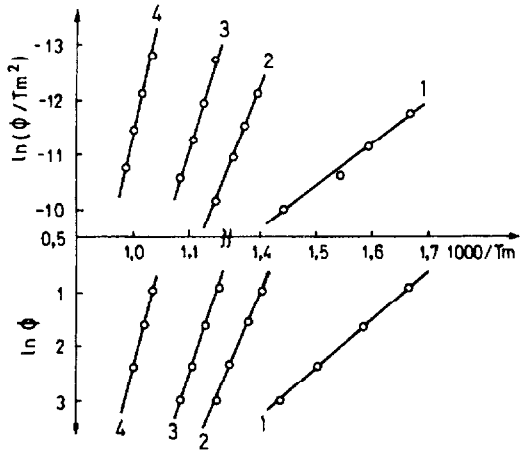

Fig. 4 Dependences $\ln(\Phi/T_m^2)=f(1/T_m)$ and $\ln\Phi=f(1/T_m)$ for the oxidation of molybdenum sulphide

The values obtained for the kinetic parameters indicate that all the processes occurring in the course of the oxidation of molybdenum sulphide are entirely within the kinetic area, which suggests that the temperature is the predominant factor influencing the process rate. Figure 5 presents the temperature dependence of the values obtained for the activation energy E.

The temperature dependence obtained indicates that during the evolution of SO_2, the crystal lattice of the starting component transforms, leading to an increase in the activation energy, and the influence of temperature on the rate of the processes occurring at higher temperatures becomes more pronounced.

Table 1 Calculated values for the activation energy and integration constants for the oxidation processes of molybdenum sulphide

Process	Method			
	Kissinger		Ozawa	
	E/kJ mol^{-1}	C	E/kJ mol^{-1}	C_1
1	67	5.54	81	$3.11 \cdot 10^{7}$
2	265	$1.09 \cdot 10^{14}$	273	$2.09 \cdot 10^{20}$
3	182	$5.09 \cdot 10^{5}$	207	$1.09 \cdot 10^{13}$
4	283	$6.48 \cdot 10^{9}$	327	$1.17 \cdot 10^{18}$

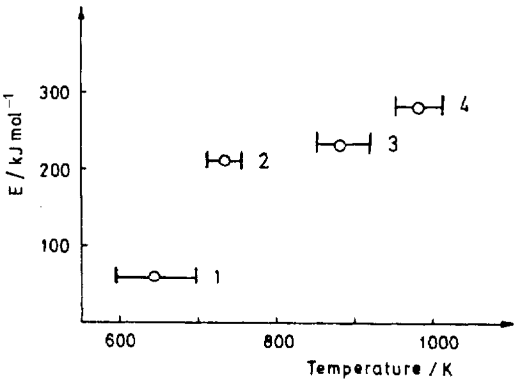

Fig. 5 The dependence $E=f(T)$ for the oxidation of molybdenum sulphide

This completes the results obtained by simultaneous DTA-TG-DTG analysis, and presents a more complete picture of the mechanism of oxidation of molybdenum sulphide in an air atmosphere than the one provided in previous publications.

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