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KINETICS AND MECHANISM OF PROCESSES IN THE SYSTEM $FeSO_4 \cdot 7H_2O-MnO_2$

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Abstract

Processes which occur during the thermal treatment of system $FeSO_4 \cdot 7H_2O-MnO_2$ are of the interest for obtaining $MnSO_4$, which can be easily soluted in water and separated from impurities in manganese slime in zinc metallurgy. Results of the experimental investigations of such processes are given in this paper. Kinetic parameters for the previously defined mechanism were determined using Borchardt and Daniels method.

Keywords: kinetics, system $FeSO_4 \cdot 7H_2O-MnO_2$

Introduction

Sulphation process of MnO, intermediate product obtained in zinc hydrometallurgy, can be used for extraction of manganese by solubilization of $MnSO_4$ originated in this process. Suitable agent for sulphation is $FeSO_4 \cdot 7H_2O$, which can be relatively simply used under industrial conditions.

Complex processes, which are the subject of this paper, are taking place during the thermal treatment of manganese oxide with ferrous sulphate.

Gallagher *et al.* [1] investigated thermal decomposition mechanism for $FeSO_4 \cdot 7H_2O$ in oxidative atmosphere and in air, while Earnest [2] investigated the same mechanism but in an inert atmosphere and in vacuum. Behaviour of MnO_2 during the heating is described in books of Mackenzie [3] and Živković and Dobovišek [4].

Investigation of $FeSO_4 \cdot 7H_2O-MnO_2$ system is of practical and theoretical importance, because it presents the basis for manganese extraction from refuse manganese slime in zinc metallurgy.

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Experimental

Manganese slime from the factory for zinc production "Zorka" Šabac (Serbia) was used in experimental investigations.

Composition of manganese slime is given: Mn – 44.8%; Pb – 3.53%; Zn – 0.10%; Ca – 0.30%; Ba – 8.20% and the rest is H_2O (manganese is in form of MnO).

$FeSO_4{\cdot}7H_2O$ of the technical purity, produced in factory "Zorka"-Šabac (Serbia) was used as a sulphation agent.

For thermal decomposition processes simultaneous DTA-TG-DTG analysis was used and preformed on a derivatograph (MOM, Budapest). Identification of the phases was carried out on an X-ray Siemens apparatus with a Cu anticathode.

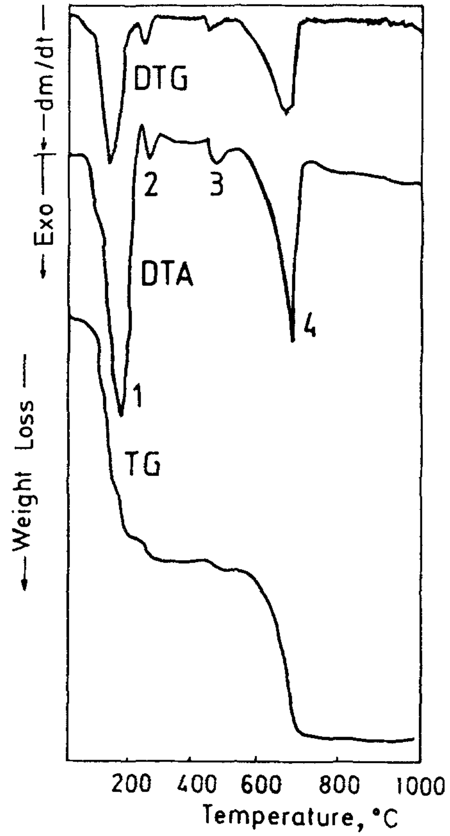

Fig. 1 DTA-TG-DTG curve for $FeSO_4{\cdot}7H_2O$ in an air atmosphere at a heating rate of 10 deg·min^{-1}; (Numbers from (1) to (4) are representing respective processes)

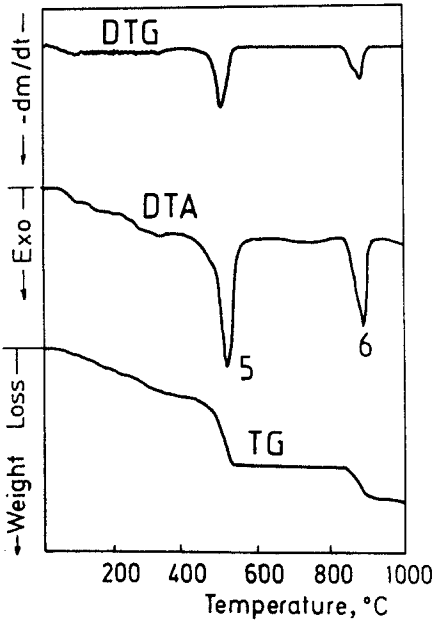

Fig. 2 DTA-TG-DTG curve for MnO_2 in an air atmosphere at a heating rate of 10 deg·min^{-1}; (Numbers (5) and (6) are representing respective processes)

Discussion

DTA-TG-DTG curves for pure components, necessary for determination of mechanism in $FeSO_4 \cdot 7H_2O$–MnO_2 system, are given in Figs 1, and 2.

Based on obtained results from Figs 1, and 2, mechanism for decomposition of the pure $FeSO_4 \cdot 7H_2O$ and MnO_2 can be defined:

a) decomposition of the $FeSO_4 \cdot 7H_2O$

$$FeSO_4 \cdot 7H_2O = FeSO_4 \cdot H_2O + 6H_2O \tag{1}$$

$$FeSO_4 \cdot H_2O + {}^1\!/\!_2O_2 = 2Fe(OH)SO_4 + H_2O \tag{2}$$

$$2Fe(OH)SO_4 = Fe_2O(SO_4)_2 + H_2O \tag{3}$$

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3, \text{ and} \tag{4}$$

b) decomposition of MnO_2

$$3MnO_2 = Mn_3O_4 + O_2 \tag{5}$$

$$Mn_3O_4 = 3MnO + {}^1\!/\!_2O_2 \tag{6}$$

Comparative DTA-TG-DTG analysis was done for the mixture $FeSO_4 \cdot 7H_2O$ and MnO_2 in the molar relation 1:1, and obtained result is given in Fig. 3. Based on the weight loss at TG curves, effect character on DTA curves and phase X-ray analysis for the samples heated at temperatures 350, 520 and 900°C, the following mechanism for processes in investigated system can be written:

$$FeSO_4 \cdot 7H_2O + MnO_2 = FeSO_4 \cdot H_2O + MnO(OH)_2 + 5H_2O \quad (7)$$

$$2FeSO_4 \cdot H_2O + MnO(OH)_2 + O_2 = 2Fe(OH)SO_4 + MnO_2 + 2H_2O \quad (8)$$

$$2Fe(OH)SO_4 + 3MnO_2 = Fe_2O(SO_4)_2 + Mn_3O_4 + H_2O + O_2 \quad (9)$$

$$FeO(SO_4)_2 + Mn_3O_4 = 6FeSO_4 + Mn_3O_4 + {}^{9}\!/_{2}O_2 \quad (10)$$

$$Mn_3O_4 = 3MnO + {}^{1}\!/_{2}O_2 \quad (11)$$

$$2FeSO_4 + MnO + O_2 = MnSO_4 + Fe_2O_3 \quad (12)$$

Kinetic analysis for the obtained results was carried out by using Borchardt and Daniels method [5], based on DTA curve shown in Fig. 3. There is over-

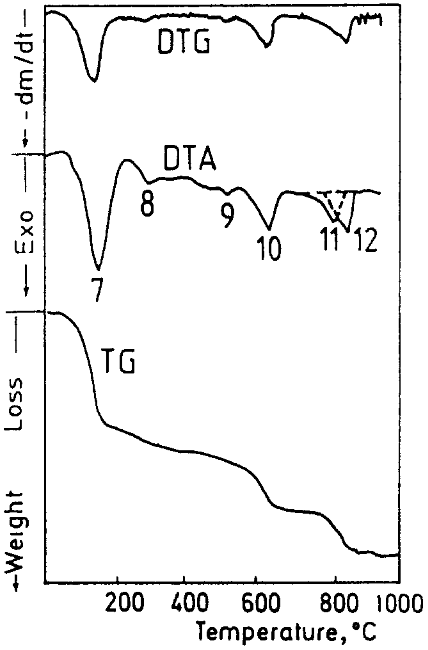

Fig. 3 DTA-TG-DTG curve for $FeSO_4 \cdot 7H_2O$–MnO_2 in an air atmosphere at a heating rate of 10 deg·min^{-1}; (Numbers from (7) to (12) are representing respective processes)

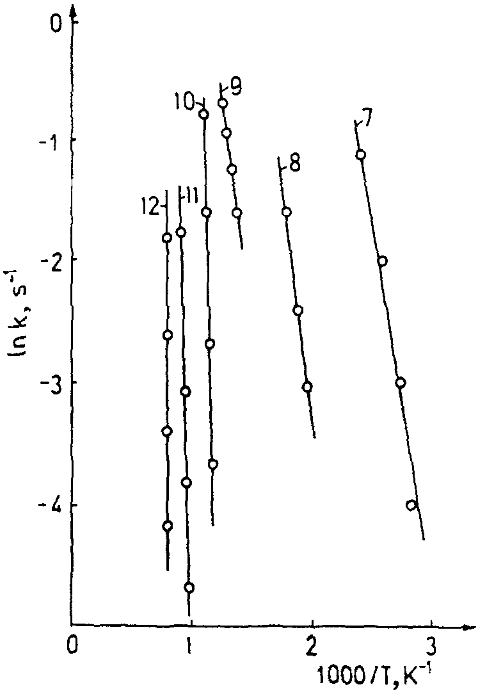

Fig. 4 Dependence log$k$ = f(1/T) for processes from (7) to (12) in system $FeSO_4 \cdot 7H_2O$–MnO_2

lapping of peaks on DTA curve for processes (11) and (12), so approximation of the DTA curve course was done as it is shown in Fig. 3.

Dependence log$k$ = f(1/T) for processes during thermal treatment of the investigated mixture $FeSO_4 \cdot 7H_2O$–MnO_2 are given in Fig. 4, and following values for activation energy are: for

process (7) E = 48 kJ/mol; for process (8) E = 67 kJ/mol; for
process (9) E = 73 kJ/mol; for process (10) E = 374 kJ/mol; for
process (11) E = 353 kJ/mol and for process (12) E = 360 kJ/mol.

Activation energy results shows that all investigated processes are within the kinetic area, which suggests that temperature is of the predominant influence on the process rate. First three processes, reactions (7), (8) and (9) which present the dehydration of $FeSO_4 \cdot 7H_2O$ and partly hydration and redehydration of MnO_2, have activation energy values in interval 50–70 kJ/mol, which indicates the similar character of these processes. Processes (10), (11) and (12) which present the decomposition of the ferrous oxisulphate and $MnSO_4$ origination and at which the oxygen is separated, have considerably higher values for activation energy in interval 350–370 kJ/mol, which indicates their complete dependence from temperature (Fig. 5).

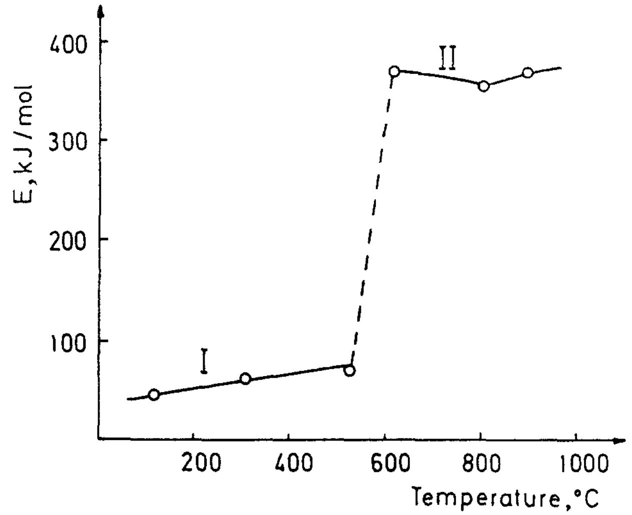

Fig. 5 Dependence of activation energy from temperature for processes in system $FeSO_4 \cdot 7H_2O-MnO_2$; (Note: I group of processes – dehydration, II group of processes – oxisulphate decomposition and sulphation)

These results show that the sulphation process of MnO_2 can be successfully carried out at temperatures about 900°C, and that the reaction rate for these processes at lower temperatures will be neglectly low.

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