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KINETIC STUDIES OF ISOTHERMAL DEHYDRATION OF COMPRESSED $Li_2SO_4 \cdot H_2O$ POWDERS

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Comparative kinetic studies of isothermal dehydration of compressed $Li_2SO_4 \cdot H_2O$ powders and single crystals indicate that in both cases the reaction rates are commensurable and agree with the kinetic behavior.

В сообщении представлены результаты экспериментального изучения кинетики изотермической дегидратации как прессованных порошков, так и монокристаллов $Li_2SO_4 \cdot H_2O$. Показано, что в обоих случаях скорости разложения соизмеримы, и наблюдается сходство в кинетическом поведении.

INTRODUCTION

As usual, experimental studies of thermal decomposition of powders

$$AB_{(s)} \rightleftharpoons S_{(s)} + B_{(g)} \tag{1}$$

do not provide reliable kinetic data, since it is very difficult to take into account heat- and mass transfer processes always taking place in finely dispersed reactants.

More reliable data are obtained from the studies of single crystals, but, unfortunately, in many cases there are no crystals of sufficient size. This problem can be solved by studying compressed powders. We believe that for such samples the reaction is to be localized in a thin layer (reaction zone). Hence the macrokinetics is simplified and a kinetic analysis can be performed in terms of the geometrical control [1]. To check this

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suggestion, we compared the data obtained with those for single crystals and with the available literature data for powders.

EXPERIMENTAL

Large crystals of $Li_2SO_4 \cdot H_2O$ were grown through slow evaporation of a saturated aqueous solution at room temperature. Plate-like, 0.1 cm thick crystals were cut from the initial crystal parallel to the (101) face by the wet-thread method. The control of the crystallographic plane was carried out on a DRON-3. Then disks (d=0.6 cm) were cut out of the plate-like crystals using a brass tube and ASM 2/3 diamond abrasive. Powders were prepared from commercial chemical grade $Li_2SO_4 \cdot H_2O$ by 5 min grinding in a mill supplied with a water cooling system. Thermal analysis (a Paulik-Paulik derivatograph) shows that under grinding no dehydration takes place, which agrees with the literature data [2]. Pellets of the same size as single crystal samples were compressed from the powders. The size of pellet particles was determined using a JSMT-20 scanning electron microscope. Isothermal dehydration of the pellets was studied by means of a quartz crystal microbalance [3] under dynamic vacuum of $P \sim 4 \times 10^{-5}$ Pa. Temperature control of the samples was accurate to ± 0.1 K.

RESULTS AND DISCUSSION

Kinetics of isothermal dehydration is presented as plots of the amount of water released from the sample, m vs. time, t (Fig. 1). It is evident that both compressed powders and single crystals are described by the linear dependence

$$m(t) = kt, \quad \text{where} \quad k = A \exp(-E/RT) \qquad (2)$$

(According to the procedure of kinetic measurements [3], the opposite face and the side surfaces were covered with an indium-gallium eutectic to avoid reaction. For this experimental geometry one-dimensional advancement of the reaction interface is realized.)

It is known that $Li_2SO_4 \cdot H_2O$ dehydration is a topochemical

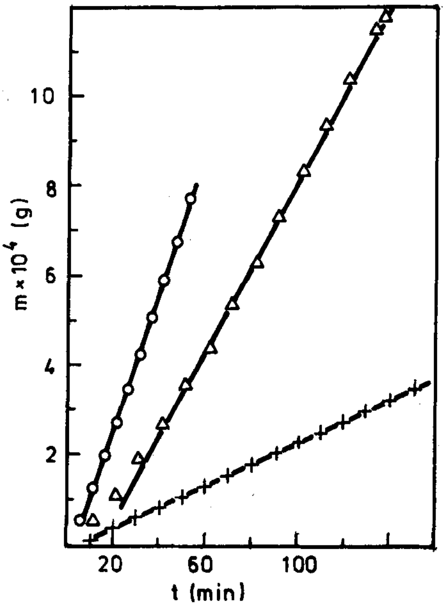

Fig. 1. Isothermal dehydration of $Li_2SO_4 \cdot H_2O$. T = 343.2± ±0.1 K. (+) - single crystal. Reaction interface is advancing in the [101] crystallographic direction. (o) and (Δ) correspond to dehydration of compressed powders. Compression pressure: (o) - 1387 mPa, (Δ) - 1734 mPa. Linear correlation coefficients: (o) - 0.9989; (Δ) - 0.9995; (+) - 0.9999

reaction [4], and the linear behavior of m(t) for single crystals is due to constant advance rate of the reaction interface into the reactant. Let us consider the dehydration of compressed powders. $Li_2SO_4 \cdot H_2O$ dehydration is a reversible process [4], hence the reaction involves the participation of only those particles, near the surface of which the concentration of unbound water molecules is significantly lower than its equilibrium value. Mass transfer of a gaseous product from the particles localized under the reacting layer, and hence, the contribution of these particles to m(t), depends on the porosity. If we assume that the pore structure depends on the compressing pressure (though this is not evident and is open for discussion), a qualitative interpretation of experimental data presented in Fig. 1, is possible. At P = 2775 mPa, dm/dt becomes comparable with the data for single crystals (Fig. 2). In our experiments the thickness of a layer of solid product in the [101] crystallographic direction was about 10^{-2} cm. This corresponds to about 250 "mono-

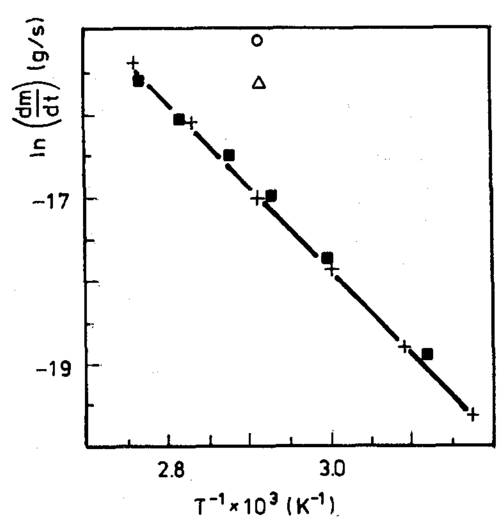

Fig. 2. Experimental data for $Li_2SO_4 \cdot H_2O$ isothermal dehydration in Arrhenius coordinates. (+) - single crystal. Reaction zone is advancing in [101] crystallographic direction. (□) - pellet compressed from powder ground in mill. Compression pressure P = 2775 mPa. Kinetic parameters calculated according to the least-squares method using eq. 2: (□) - E=(18.8 0.5) kcal/mol, ln A=(10.6 0.7); (+) - (20.3 0.2) kcal/mol, ln A=(12.8 0.2). Points (o) and (Δ) were calculated according to the least-squares method from the kinetic data of Fig. 1

layers" of particles in pellets with the same fractional decomposition, because the average particle size is 4×10^{-5} cm (Fig.3).

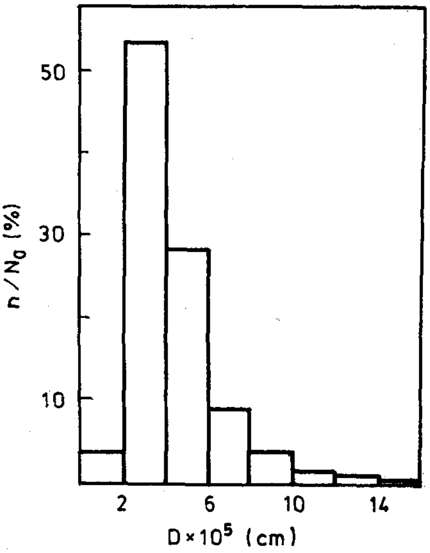

Fig. 3. Size distribution of particles in compressed pellet according to SEM data (N_0=923 particles)

The quantity of particle layers for the compressed powders taking part in the reaction simultaneously, could be considered as a "reaction zone". Under dehydration this reaction zone moves into the pellet at a constant rate. In accordance with the data presented in Fig. 1, the upper value for the size of the reaction zone amounts to $d \ll 10^{-2}$cm.

It is of interest to compare the results obtained with the data of Ref. [5], where the author examined the dehydration kinetics of $Li_2SO_4 \cdot H_2O$ powders charged into a crucible, in a dry nitrogen flow. It is well known [1] that the rate of reaction 1 depends on both the pressure and the composition of the gaseous atmosphere in the reactor. Hence to compare our data for dm/dt with those from Ref. [5] is incorrect. It is reasonable to compare the kinetic behavior.

In accordance with his kinetic analysis [5], the author suggests that the $Li_2SO_4 \cdot H_2O$ dehydration is described by the Avrami-Erofeev equation. In our case the dehydration of both single crystals and powders is described by linear relationship 2 . It must be noted that the kinetic data obtained in studying the thermal decomposition of compressed powders agree with those for single crystals. It is necessary, however, to carry out more careful investigations in order to clarify differences in their kinetic parameters (Fig. 2) and to obtain a more accurate quantitative description for the decomposition kinetics of compressed powders. The results of our further investigations will be published elsewhere.

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