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KINETICS OF TRANSFORMATION OF CHAINS IN AMORPHOUS SULPHUR DOPED WITH PHOSPHORUS

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Abstract

The transformation rate of the chains in amorphous sulphur doped with 0.43, 0.86 and 1.28% at. P was examined by calorimetric method at 298 K. The samples were remelted at T_f=443 K. For description of the results the equation $X=1-\exp[-(kt)^z]$ was used (X – transformation degree, t – time, k and z – constants). The admixtures of phosphorus inhibit the transformation strongly. The constants k and z are less smaller for the samples S+P than for pure sulphur.

Samples S+1.28% at. P were examined in the range of the temperatures from 203 to 308 K. The activation energy is equal to E=86.6 kJ mol^{-1} with standard error S_E=12.0 kJ mol^{-1}.

The effect of the admixture of phosphorus on the kinetics of the nucleation and the growth of the nuclei was discussed.

Keywords: amorphous sulphur, kinetics of transformation

Introduction

Amorphous sulphur is formed by quenching of liquid sulphur. When the temperature of liquid sulphur, T_f, is higher than 432 K (i.e. the temperature at which the polymerisation $n/8\ S_8$ (ring) $\rightarrow S_n$ (chain) occurs) in the freshly obtained amorphous sample an exothermic process progresses quickly [1–5]. The kinetics of the process is expressed by the equation of Avrami and Erofeev [6 –8]. Its activation energy is E=21 kJ mol^{-1} [2].

The increase of the temperature of liquid sulphur, T_f, diminishes the rate of the process and the amount of the formed product [3, 4]. The admixtures of selenium have a simultaneous effect [5].

It is expected that the chains in amorphous sulphur are packed more or less parallelly [9]. It seems that such packing is necessary for the occurrence of the investigated process, whose product is an unstable modification containing the chains [1–5]. Probably, this modification changes into orthorombic sulphur composed of ordered octaatomic rings.

During the melting of the mixture of sulphur and phosphorus $-S-P<^{S-}_{S-}$ bonds are formed and the chains become space – branched and their parallel packing is disturbed strongly [10]. Thus, the admixtures of phosphorus inhibit the examined proc-

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ess [1]. The kinetics of the transformation of the chains in the S+P – samples has not been examined. Such studies should give a new information on the nature of discussed process.

Experimental

The studies were made by means of a calorimetric method. The calorimeter and the measurement method have been described earlier [2]. The method of preparation of the S+P – samples is given in [1].

Results

Effect of concentration of phosphorus

The samples doped with 0.43, 0.86 and 1.28% at. P, remelted at T_f=443 K, were examined by means of a calorimetric method at a temperature of 298 K. The recorder sensitivity and the paper travel were equal to 0.00532 K mm^{-1} and 25 mm min^{-1}, respectively. As a result of the measurement the temperature T_c of the calorimetric cell *vs.* time t curve was obtained [2–5]. Based on the $T_c=f(t)$ curves the transformation degrees X *vs.* time t were calculated

$$X = \frac{Qt}{Q} \tag{1}$$

where Q_t and Q – are heats evolved by 1 g of sample during time t and $t=\infty$ respectively.

The typical curves $X=f(t)$ for pure (0% at. P) sulphur (data from [2]) and for the samples doped with 0.43, 0.86 and 1.29% at. P are presented in Fig. 1.

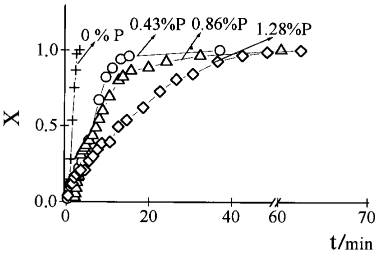

Fig. 1 Degrees of transformation of chains, X *vs.* time t for amorphous sulphur doped with phosphorus (% atomic fraction)

The diagram illustrates that the admixtures of phosphorus strongly decrease the rate of the transformation (if the quantity of phosphorus was larger than 1.28% at. P, the process was not observed at 298 K).

The results were treated by the equation of Avrami and Erofeev [8–10]

$$\lg[-\lg(1-X)]=z\lg k+z\lg t-\lg 2.303 \tag{2}$$

where k and z – constants.

The typical dependencies lg[–lg(1–X)]=f(lg$t$) for the samples S and S+1.28% at. P are given in Fig. 2. It is seen that the results fit the above equation.

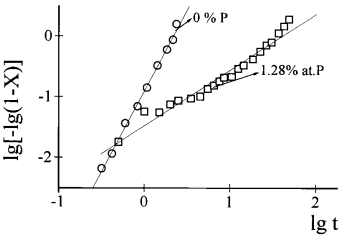

Fig. 2 Values lg[–lg(1–X)] *vs.* lg$t$ for transformation of amorphous samples S and S+1.28% at. P at 298 K

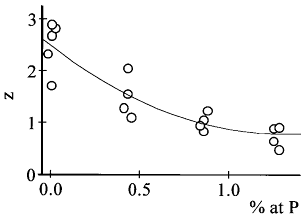

Fig. 3 Values z *vs.* quantity of admixtures of phosphorus at 298 K

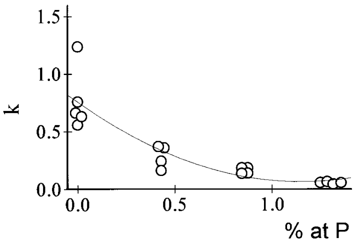

Fig. 4 Values k *vs.* quantity of admixtures of phosphorus at 298 K

The calculated values k and z for all examined samples are presented in Figs 3 and 4.

It is seen that the admixture of phosphorus decreases the values z and k.

Determination of the activation energy

Amorphous sulphur samples doped with 1.28% at. P were examined at temperatures T=293, 298, 303 and 308 K. All samples were remelted at temperature T_f=443 K. The typical dependencies lg[–lg(1–X)]=f(lg$t$) for the transformation temperatures 293 and 308 K are presented in Fig. 5.

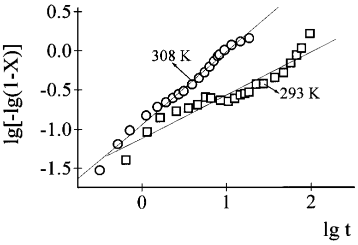

Fig. 5 Values lg[–lg(1–*X*)] *vs.* lg*t* for the transformation of amorphous sulphur with 1.28% at. P at 293 and 308 K

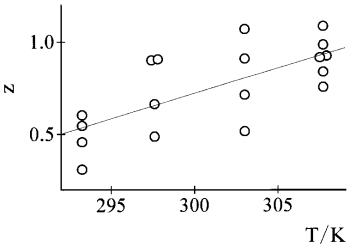

Fig. 6 Value *z vs.* process temperature for amorphous sulphur doped with 1.28% at. P

The values *z* and lg*k* for all examined samples S+1.28% at. P are presented in Figs 6 and 7. The value *z* increases with the temperature *T* of the process (Fig. 6).

The slope of the linear dependence of the value *z vs.* process temperature *T* is equal to b=0.02732 K^{-1} with standard S_b=0.0073 K^{-1}. At a significance level of 0.01 it is assumed that the slope is not equal to zero.

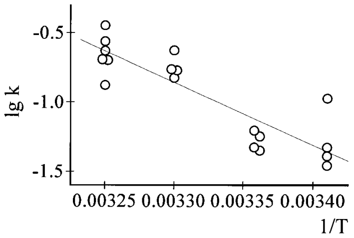

Fig. 7 Arrhenius slope for transformation of amorphous sulphur doped with 1.28% at. P

The function lg*k vs.* the reciprocal temperature *T* of the process (Fig. 7) is linear. Its slope is equal to b=–4522.0 K with standard error S_b=628.5 K. After multiplication of these values by the number 2.303 and by the gas constant the activation energy E=86.6 kJ mol^{-1} was obtained with standard error S_E=12.0 kJ mol^{-1}. The mean value $\bar{z}$ in the temperature range from 293 to 308 K is equal to 0.753 with an error of 0.0535.

Discussion

The admixture of phosphorus decreases the values z and k in Eq. (2).

These results may be explained as follows. The transformation of the chains processes in the stages of the formation and growth of the nuclei [1–5]. They are formed during consecutive processes in the transformation centres, i.e. in the microregions where the chain fragments are arranged more or less parallelly and their atoms are ordered adequately [1–5]. The constant z is given by [6–8]

$$z = i + \sum_{1}^{3} \chi_{\mathrm{h}} \tag{3}$$

where i – is a value depending on the number of slowly progressing processes of the nucleation, χ_{h} – is the exponent in the equation

$$r_{\mathrm{h}} = c_{\mathrm{h}}(t - y)^{\chi_{\mathrm{h}}} \tag{4}$$

r_{h} and c_{h} – are the dimensions of the growing grain and its coefficient of linear growth in the definite space direction **X**, **Y** or **Z**, t – is the duration of the transformation, y – the moment of the breaking of the nucleus formation.

The less ordered the structure of the centre, the higher is the value of i [8]. Probably, a parallel configuration of the chains and an adequate arrangement of their atoms are necessary for the growth of the nuclei [1–5, 8]. The better this arrangement around the formed nucleus and the larger the area over which it spreads out, the faster the grain grows and the larger the size it attains higher, to which a higher value of $\sum_{1}^{3}\chi_{\mathrm{h}}$ corresponds [2, 3, 5].

The rate constant k is given by [6–8]

$$k = \left(\mathrm{const} \prod_{1}^{\mathrm{i}} k_{\mathrm{k}} \prod_{1}^{3} c_{\mathrm{h}} \right)^{\frac{1}{z}} \tag{5}$$

where L – number of the nucleation centres, k_{k} – rate constant of the slow process of formation, c_{h} – coefficient of linear growth of the nucleus.

In amorphous sulphur doped with phosphorus there are $-\mathrm{S}-\mathrm{P}<^{\mathrm{S}-}_{\mathrm{S}-}$ bonds [10]. Thus the chains become space – branched, what disturbs its parallel packing strongly. Consequently, the number L of the nucleation centres decreases, which causes the decrease in the value of k (formula 5).

Probably, the dimensions of the adequately arranged regions, in which the stable nuclei can grow, decrease too. Thus, the grains of the product phase in amorphous sulphur attain smaller sizes, i.e., the value of $\sum_{1}^{3}\chi_h$ and, consequently, the coefficient *z* decrease (formula 3).

The increase of the process temperature increases in the value of *z* (Fig. 6). This increase in the value of *z* is in accordance with earlier results [2, 5]. Probably, the increase of the process temperature causes an increase in the sizes of the product grains, i.e., the value $\sum_{1}^{3}\chi_h$ (formula 3) and consequently the value *z* increase.

For the samples doped with 1.28% at. P the activation energy *E* and the mean value $\bar{z}$ are measured with relatively large errors. The product $\bar{z}E$, which can be used in the discussion of the results [5, 8] has a relatively large error. It was not taken into account in the discussion, because the conclusions would not be convincing.

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