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THERMAL DECOMPOSITION OF COPPER HYPOPHOSPHITE AND POSSIBILITY OF THE REACTION CONTROL

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ABSTRACT

Topochemical reaction of copper hypophosphite thermal decomposition under non-isothermal and isothermal conditions was investigated. Regulation methods of the main kinetic parameters (rates of nucleation and growth) are proposed.

INTRODUCTION

Thermal decomposition of copper hypophosphite is a basis of new methods of scantyoperational palladiumless metallization of dielectrics [1]. Kinetics of the reaction is characterized by the nucleation rate (or the length of an induction period) and by the growth rate (rate of an interface movement). The aim of this work is to investigate the kinetics of the reaction and the possibility of its control.

EXPERIMENTAL

The reaction was investigated by means of thermal analyser of Paulic type and thermogravimetric kinetic device with sensitivity 10^{-6}g and thermal stability ±0.2°C. Crystals of copper hypophosphite were prepared according to [2] from water solution. Doping was carried out by an acid and co-crystallization into synthetic solutions. The time when the decomposition degree reached the value 0.05 was accepted as a length of an induction period. Decomposition of copper hypophosphite layers with thickness 10mμ was carried out on triacetic plates, which were treated by phosphorous acid. The rate of an interface movement was detected by direct microscopic measurements.

RESULTS AND DISCUSSION

Decomposition of copper hypophosphite in mixture with quartz sand with the relation 1:1 (heating rate 0.6°/min in the region 20-130°C in the air) is listed in Fig.1.

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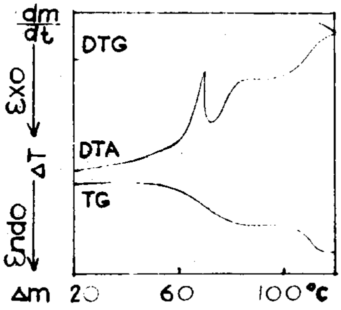

Fig. 1.

According to 3 the decomposition begins under the temperature 50°C:

$$Cu(H_2PO_2)_2 \rightarrow Cu + H_3PO_2 + \frac{1}{2}P_2O_3 + \frac{1}{2}H_2O$$

If the temperature is higher than 90°C, the decomposition of hypophosphorous acid is observed. Decomposition of copper hypophosphite consists of two stages. The first stage is characterized by a sharp exothermic effect and a slight change of weight. Essential decrease of a sample weight takes place in the second stage and an exothermic effect is unsignificant. The slight change of a sample weight in the first stage can be explained by a partial pass of the second stage due to local superheating provoked by a sharp exothermic effect in the first stage.

A decrease of a quartz quantity in mixture leads to the reaction transition at the first stage in the explosive regime.

Kinetic curves of copper hypophosphite decomposition under isothermal conditions in the temperature interval 45-60°C are characterized by significant induction periods. Effective activation energies of the decomposition process are equal: 23.8±1.2 kcal/mole from maximum rates; 26.6±1.4 kcal/mole from induction periods.

Possible mechanism of the decomposition reaction is presented in[4]. The formation of a molecule of hypophosphorous acid with a third-coordinated phosphorus is the reaction of nucleation.

$$H^+ + H_2PO_2^- \rightarrow H_3PO_2$$

Growth of the phase products is provided by generation of increasing quantities of acid at the interface:

$$H_3PO_2 + Cu^{2+} \rightarrow Cu + \frac{1}{2}P_2O_3 + \frac{1}{2}H_2O + 2H^+$$

The first stage of decomposition with sharp exothermic effect is considered to be connected with this chain process.

Nucleation rate can be changed by an acid introduction into the crystals of copper hypophosphite. Introduction of hypophosphorous acid into the crystallization solution of copper hypophosphite was shown to decrease the length of an induction period at further decomposition. Empirical dependence of the induction period length upon the concentration of acid introduction C (mole/l) is presented by equation $\tau = \tau_0 - AC^2$, where τ_0 - length of induction period of crystal decomposition without additions, equal to 129 min, A = 5.86 $(\text{mole/l})^{-2}$.

Dependence of nucleation rate $\frac{1}{\tau}$ (min^{-1}) upon acid concentration Ci introduced (mole of acid/mole of hypophosphite) is presented in Fig.2.

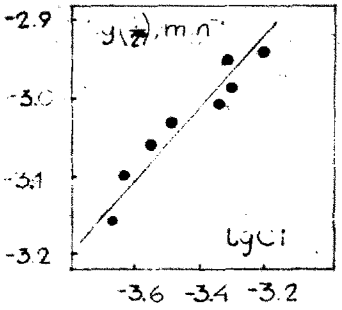

Fig. 2.

According to[4], an enhanced acid concentration is near the reagent-product interface in the partially decomposed crystals. Probably, this fact defines the development of the reaction by the way of the interface movement. In this case one can control the rate of the interface movement by varying the conditions of the acid removal from the region near the interface.

Dependence of the interface position on time of decomposition is presented in Fig. 3. The samples were thin solid layers of copper hypophosphite on the triacetic plates untreated (a) and treated by phosphorous acid (b). Temperature is 50°C.

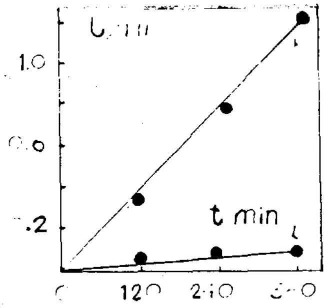

Fig. 3.

Thus, in case of topochemical decomposition of copper hypophosphite thin layers the rate of the interface movement can be changed by acidity of the plate under other equal conditions.

CONCLUSIONS

1. Thermal decomposition of copper hypophosphite under non-isothermal and isothermal conditions was investigated. Kinetics of this topochemical reaction is detected by 2 main parameters - rate of nucleation and rate of interface movement.

2. Methods of control of these parameters are proposed by means of acid introduction into crystals and by changing the acidity of the plate, on which crystallic layer is decomposed.

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