

INVESTIGATION OF THE ACID DISTRIBUTION NEAR THE REACTANT—PRODUCT INTERFACE DURING THE THERMAL DECOMPOSITION OF COPPER HYPOPHOSPHITE THIN LAYERS

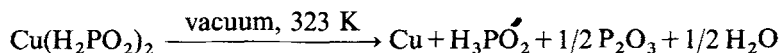
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During the decomposition of thin layers of copper hypophosphite on a plate, an increased concentration of the active product of the reaction (acid) may be observed near the reactant—product interface. The acid profile near the interface widens on increase of the decomposition temperature. The profile can also be widened by reducing the efficiency of acid removal to the plate by its preliminary acid saturation. In both cases the rate of interface propagation is increased. The increased reactivity of copper hypophosphite near the interface, and the technological character of the decomposition reaction, are caused by acid diffusion from the reaction product into non-reacted parts of the substance.

The thermal decomposition of copper hypophosphite is a topochemical reaction: it proceeds via the formation and growth of product nuclei. The products of decomposition have been determined by different methods: copper by X-ray analysis and electron diffraction. Products with high vapour densities (hypophosphorus acid, phosphorus trioxide, water) were found by mass-spectroscopy during the process. The presence of hypophosphorus acid and phosphorus(III) compounds was shown by chemical analysis. It is possible that the phosphorus-containing products in the condensed form are a mixture of hypophosphorus acid, phosphorus acid and phosphorus trioxide. The reaction equation is as follows [1]:



What is the reason for the topochemical character of the reaction? Why is the reactivity of copper hypophosphite higher near the reagent—product interface?

It was earlier supposed that the reason for the changing reactivity is the formation and accumulation in this region of hypophosphorus acid, which is an active reaction product [2]. It was subsequently demonstrated that during the

decomposition of single-crystals of copper hypophosphite there actually is an increase in the concentration of acid near the interface [3]. There is probably a connection between the rate of interface movement and the distribution of the acid. The aim of this study is to investigate the distribution of acid near the interface during the decomposition of copper hypophosphite layers, by means of electroconductivity measurement in this region, and to study whether there is a correlation between the rate of interface movement and the acid distribution. The decomposition of a copper hypophosphite layer on a plate surface differs from that of a single-crystal. The acid formed in the reaction may diffuse not only into the non-decomposed part of the layer, but also into the plate. The acid on the plate is adsorbed by the material of the plate or chemically interacts with it, with no resulting decomposition of copper hypophosphite.

The efficiency of acid removal to the plate may be varied by preliminary saturation of the plate with acid.

A change in acidity of the plate influences the concentration of an active decomposition product near the interface and the rate of interface propagation. These effects can occur if the thickness of the copper hypophosphite layer is not greater than that of the acid distribution near the interface: $\sim 100 \mu\text{m}$. Otherwise, the acid cannot diffuse from the upper part of the layer to the plate. The plate has no essential influence on the decomposition of thick layers.

Experimental and discussion

Copper hypophosphite layers were produced by transferring copper hypophosphite solution onto a cellulose triacetate plate, followed by centrifugation and simultaneous drying. The thickness of the layers produced in this way was 20–30 μm .

The kinetics of movement of the reactant—product interface was studied. The interface position relative to the initial one was determined with an object-micrometer. The rate of interface advance was shown to be constant in time. This allows the supposition that the interface is a stationary formation and that the processes at the interface, e.g. the diffusion of acid, are steady-state processes. From the temperature-dependence of the rate of interface movement, the effective activation energy was determined to be $E_{\text{act}} = 147 \pm 21 \text{ kJ/mole}$.

The acid distribution near the reactant—product interface was studied by measurement of the surface electric conduction near the interface. A two-electrode measuring system was used. The electrodes were produced after preparation of the copper hypophosphite layer and were situated 0.5–1 mm from the optically observed interface.

During the interface movement towards the electrodes, the change in electro-conductivity caused by the change in acid concentration was measured.

The electric conduction of copper hypophosphite is of proton character. The electric conduction of copper hypophosphite doped with acid has been shown to be determined by the acid concentration. The ratio of the surface electric conduction at different parts of a layer, depending on the distance between the interface and the point of measurement, is proportional to the ratio of the acid concentrations at the parts in question.

Besides the acid, the main product of copper hypophosphite decomposition is metallic copper, which can affect the electric conduction. We studied the changes in electric conduction during the transport of pure hypophosphorus acid along a cellulose triacetate plate to electrodes in the absence of metallic copper. In this case, the term "acid transport" means the spreading of acid over the surface, accompanied by acid diffusion inside, and acid interaction with the material of the plate. The character of the electric conduction was found to be the same for the two cases: the transport of pure acid to the electrodes, and the interface movement to the electrodes. Thus, it can be concluded that the change in electric conduction observed during the movement of the reaction interface to the electrodes is due to the change in acid concentration.

The acid distribution during the decomposition of copper hypophosphite layers at different temperatures is shown in Fig. 1. Broadening of the distribution is observed as the interface advance rate increases. In every experiment, at least seven

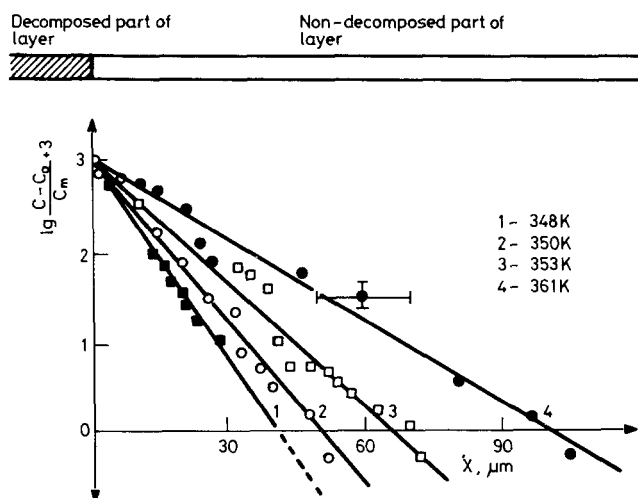


Fig. 1 Acid distribution near the interface during decomposition of copper hypophosphite layers at different temperatures

plates were investigated at fixed temperatures. The experimental error was not more than 25%. This correlates with the error in the determination of the rate of interface movement. It remains to be considered that the distribution of acid at a given temperature is stationary, i.e. $\frac{dC}{dt} = 0$. For the treatment of acid distribution from a moving interface, we used the equation:

$$-D \frac{d^2C}{dx^2} - U \frac{dC}{dx} = \frac{dC}{dt} = 0, \quad (1)$$

where D is the diffusion coefficient of acid in the layer, U is the rate of interface movement, C is the concentration of acid, in mole per cm^2 , in the layer, and x is the distance from the interface. The solution of this equation with the limiting conditions $C_{x=\infty} = C_0$ and $C_{x=0} = C_m$ is:

$$C = C_0 + C_m \cdot \exp\left(-\frac{U}{D} \cdot x\right) \quad (2)$$

From the slopes of the straight lines, it is easy to determine the diffusion coefficient for different temperatures of decomposition. The calculated value of the effective activation energy of the diffusion process is $E_D = 167 \pm 21$ kJ/mole.

It was earlier shown [4] that an increase in concentration of the acid on the plate (provided all other conditions are identical) leads to an increase in the rate of interface movement. Preliminary treatment of the plate with acid reduces the efficiency of hypophosphorus acid removal from the reaction zone. How does the acid distribution change in this case? Samples more or less saturated with acid by

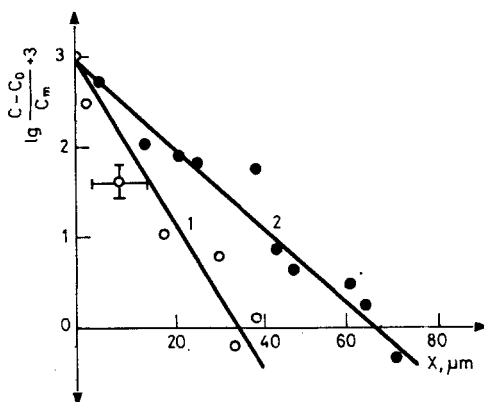


Fig. 2 Acid distribution near the interface during decomposition of copper hypophosphite layers on the plate: (1) decomposition on the starting plate; (2) decomposition on the plate previously treated with 50% phosphorous acid

treatment with aqueous acid solutions of different concentrations were used in the experiments. A layer of solid copper hypophosphite was then formed on the treated plate and the decomposition of this layer and the distribution of hypophosphorus acid near the interface were studied. Figure 2 shows the acid distribution near the interface during the decomposition of copper hypophosphite layer on various plates at 363 K; (1) decomposition on the starting plate; (2) decomposition on the plate previously treated with 50% phosphorus acid. Analogous results were obtained with hypophosphoric and sulphuric acids. It was earlier demonstrated that elevation of the decomposition temperature results in enlargement of the width of the acid distribution near the copper hypophosphite crystal—decomposition product interface, and the rate of interface propagation is also increased. The increase in the rate of the interface movement caused by an increase of plate acidity clearly also leads to a broadening of the acid distribution. Thus, an increase in the concentration of an active decomposition product near the interface results in an increase in reactivity of solid copper hypophosphite and causes the reaction to occur, mainly because of propagation of the reactant—product interface.

Basic results

1. An increase in acid concentration takes place near the reactant—product interface during the decomposition of copper hypophosphite layers.

2. The broadening of the acid distribution caused both by an increase of decomposition temperature and by an increase of plate acidity leads to a higher rate of interface movement.

3. The effective activation energy of interface movement was determined to be $E_{act} = 147 \pm 21$ kJ/mole, and the effective activation energy of diffusion of acid was $E_D = 167 \pm 21$ kJ/mole.

4. The change in the reactivity of the starting copper hypophosphite layer near the interface was determined by the formation of acid, which is a chemically active reaction product in this region.

References

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Zusammenfassung — Während der Zersetzung dünner Schichten Kupferhypophosphit kann in der Umgebung der Reaktand—Reaktionsprodukt Grenzfläche eine erhöhte Konzentration des aktiven Produktes der Reaktion (Säure) beobachtet werden. Die Säurezone in der Umgebung der Grenzfläche wird mit zunehmender Temperatur breiter. Diese Zone kann auch durch Verringern der Wirksamkeit der Säureentfernung in Richtung Träger durch dessen vorangehende Säuresättigung verbreitert werden. In beiden Fällen ist die Geschwindigkeit des Grenzflächenzuwachses erhöht. Die erhöhte Reaktivität von Kupferhypophosphit in der Umgebung der Grenzfläche sowie der technologische Charakter der Zersetzungsreaktion wird durch Säurediffusion von den Reaktionsprodukten in noch unreaktierte Zonen der Substanzen verursacht.

Резюме — Во время разложения тонких слоев гипофосфита меди на пластинке на границе раздела реагент—продукт можно было наблюдать увеличение концентрации кислоты, как активного продукта реакции. Уширение концентрационного профиля кислоты на границе раздела происходит при увеличении температуры разложения. Профили могут быть уширены и понижением выхода кислоты, удаляя предварительно насыщенную кислотой пластинку. В обоих случаях скорость распространения на границе раздела увеличивается. Увеличение реакционной способности гипофосфита меди на границе раздела и технологический характер реакции разложения обусловлены диффузией кислоты от реакционного продукта на непрореагировавшие части вещества.