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THERMOGRAVIMETRIC STUDIES OF THE DECOMPOSITION OF RED LEAD (Pb_3O_4)

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TG measurements have been performed on red lead under (a) isothermal (b) dynamic conditions, under a constant flow of nitrogen.

The results have been analyzed to establish the decomposition kinetics and calculate the activation energies.

In the case of isothermal decomposition, it is concluded that rate of diffusion of gaseous products is the controlling factor, while in dynamic decomposition nucleation and growth within the Pb_3O_4 particles is important.

Mixtures of red lead (Pb_3O_4) and silicon (Si) have commercial and military applications as delay compositions for use mainly as fuses. It is of importance to understand the burning characteristics of Pb_3O_4/Si mixtures of differing composition. DTA studies have been carried out on the mixtures by Al-Kazraji and Rees [1], and also on PbO/Si mixtures [2].

To complement these studies a detailed TG analysis of Pb_3O_4, under both isothermal and dynamic conditions, was undertaken and the results analyzed by the method developed by Doulah [3].

Experimental

A Perkin–Elmer TGS-2 apparatus was used for measuring the weight loss of the sample as it was subjected to controlled conditions. Approximately 20 mg samples were used and TG was performed under a constant flow of dry nitrogen (25cc/min) in both isothermal and dynamic conditions.

For the isothermal study, temperature ranged from 520–580°, while for the dynamic study, the rate of heating was varied from 5°/min to 40°/min.

Decomposition kinetics

The solid decomposition of the form

$$X(s) \rightarrow Y(s) + Z(g)$$

can be studied by weight loss of the gaseous products and the rate of decomposition can be represented by the equation

$$\frac{d\alpha}{dt} = Kf(\alpha) \tag{1}$$

where $f(\alpha)$ is the function of the decomposition extent α, and K is the rate constant which is expressed by the Arrhenius law

$$K = K_0 e^{-E/RT} \tag{2}$$

where E is the activation energy, K_0 the pre-exponential factor, R the gas constant and T the temperature.

It has been shown [3] that $d\alpha/dt$ can be expressed by

$$\frac{d\alpha}{dt} = \left(\frac{\beta}{\gamma}\right)\left(\frac{t}{\gamma}\right)^{\beta-1}(1-\alpha) \tag{3}$$

to yield, after integration the function

$$\alpha = 1 - e^{-\left(\frac{t}{\gamma}\right)^{\beta}} \tag{4}$$

where β and γ are parametric constants which can be determined experimentally.

Equation (4) can be linearized by expressing it in logarithmic form

$$\ln\ln\left(\frac{1}{1-\alpha}\right) = \beta \ln t - \beta \ln \gamma\,. \tag{5}$$

By use of this equation β can be obtained from the slope of a straight line that should result when the data are plotted as $\ln\ln\frac{1}{1-\alpha}$ vs. $\ln t$, and γ can be found from the intercept of the straight line.

Comparison of Eqs (1) and (3) shows that

$$K = (\beta/\gamma).$$

Application of the Arrhenius law gives

$$\ln(\beta/\gamma) = \frac{-E}{RT_{0.63}} + \ln K_0 \tag{6}$$

where $T_{0.63}$ is the temperature corresponding to $\alpha = 0.63$ at which, as was shown, Eqs (4) and (1) coincide.

For isothermal decomposition, $T_{0.63}$ is taken to be the same as decomposition temperature. For the case of decomposition under dynamic conditions, $T_{0\text{-}63}$

was determined from $\alpha - T$ measurements and the temperature was varied linearly with time, t.

Results and discussion

The results of isothermal decomposition of Pb_3O_4 at four temperatures are given in Fig. 1 showing the change of α with time.

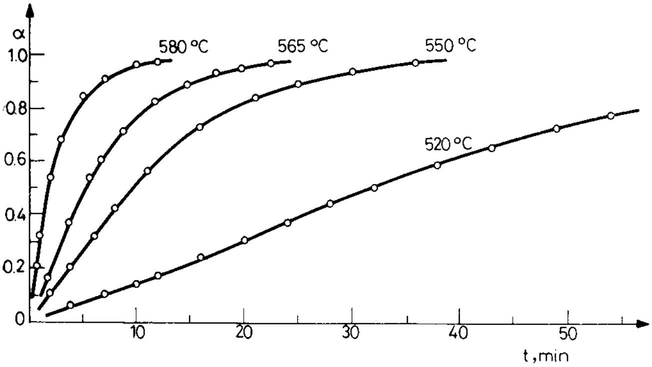

Fig. 1. α *versus* t for Pb_3O_4 (isothermal)

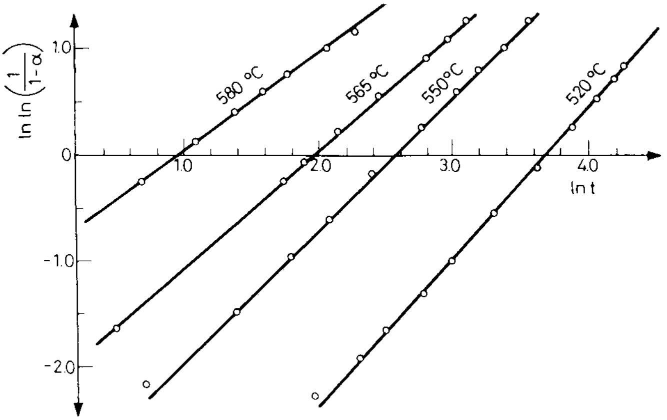

Fig. 2. lnln $\left(\frac{1}{1-\alpha}\right)$ versus ln t (isothermal)

To check Eq. (5) the results were plotted as lnln $(T/1 - \alpha)$ *vs.* ln t in Fig. 2 which shows that the data agree with Eq. (5) very well. The values of β and γ for the decomposition temperatures are given in Table 1. In Fig. 5 ln (β/γ) is drawn versus $1/T_{0.63}$, which gives a linear fit for the data satisfying the Arrhenius law with an activation energy of 240 kJ/mol.

Results obtained under dynamic conditions are shown in Fig. 4 indicating change of α *vs.* temperature at different heating rates.

In Fig. 5, t has been calculated from the relationship

$$t = (T - T_0)/\Theta$$

where Θ is the rate of temperature rise from T_0 to T. The values of β, γ and $T_{0.63}$ are given in Table 1.

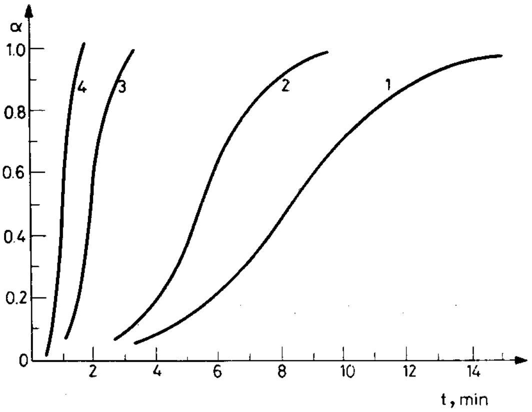

Fig. 3. α *versus* t for Pb_3O_4 (dynamic). Heating rate: 1. 5°/min; 2. 10°/min; 3. 40°/min; 4. 80°/min

The plot of $\ln(\beta/\gamma)$ versus $1/T_{0.63}$ is given in Fig. 3 which indicates reasonable agreement with the Arrhenius law. The activation energy is found in this case to be 282.7 kJ/mol.

As can be seen the activation energy of the decomposition of Pb_3O_4, under isothermal and dynamic conditions, is different. These results may be interpreted in the light of the mechanism of decomposition.

This is done by applying Eq. (4) to various model functions developed on the concept of solid state reactions. It has been found that when $\beta = 1$, decomposi-

Table 1

Results for the decomposition of Pb_3O_4

Isothermal		Dynamic	
Temp., K	β	Heating rate °/min	β
793	1.25	5	3.08
823	1.23	10	3.5
838	1.08	40	4.0
853	0.97	80	4.7

tion follows a first order decay law, $1 < \beta \leq 3$, and rate of decomposition is controlled by the rate of progress of product boundary. When $\beta > 3$ it indicates nucleation and growth type decomposition expressed by Mampel's power laws, and when $\beta < 1$ the rate of diffusion of gaseous products is the controlling step in the decomposition process.

β values, for the decomposition of Pb_3O_4 at 793 and 823 K, indicate a reaction mode that occurs mainly at the interface between the product layer and the un-

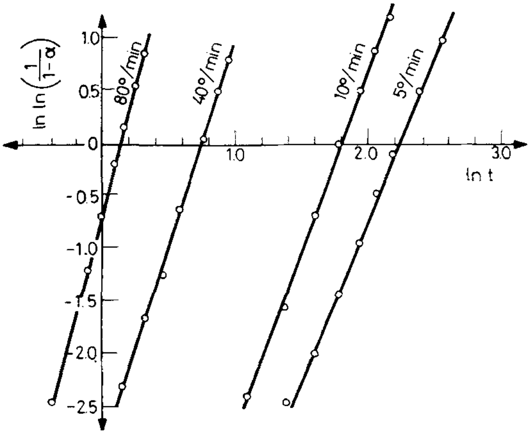

Fig. 4. lnln $\left(\frac{1}{1-\alpha}\right)$ *versus* ln t (dynamic)

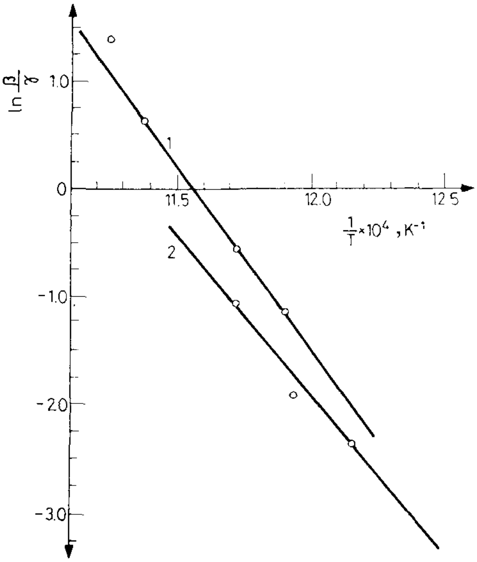

Fig. 5. ln $\left(\frac{\beta}{\gamma}\right)$ *versus* $\frac{1}{T}$ for Pb_3O_4. 1 Dynamic; 2 Isothermal

reacted part of the Pb_3O_4 particles, with a rate controlling step being the rate of progress of the interface. If this rate is faster than that of nucleation and growth, the decomposition is obviously controlled by the rate of nuclei formation which follows a first order law and has $\beta = 1$. The decomposition at 838 K is found to approach this situation.

When the surface growth of nuclei is very rapid, the product layer formed becomes thick at the initial stage of decomposition. Further decomposition depends on the rate of diffusion of gaseous products. It appears that the decomposition of Pb_3O_4 at 853 K conforms to this form of decomposition with $\beta = 0.97$.

β values obtained for the decomposition under dynamic conditions are found to be different from those for isothermal decomposition. For $\beta > 3$ this corresponds to the mechanism of decomposition in which nucleation and growth occur at different localities in the Pb_3O_4 particles without the overlapping of nuclei. As this mechanism is different from that for the isothermal case it is expected that the activation energy would be different, and is in fact larger.

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RÉSUMÉ — On a effectué des mesures TG sur du cinabre en conditions a) isothermes et b) dynamiques, sous courant constant d'azote. On a analysé les résultats afin d'établir la cinétique de la décomposition et de calculer les énergies d'activation. Dans le cas de la décomposition isotherme, on a conclu que la vitesse de la diffusion des produits gazeux était le facteur contrôlant la réaction, tandis que lors de la décomposition dynamique la nucléation et la croissance des particules de Pb_3O_4 jouaient un rôle important.

ZUSAMMENFASSUNG — TG-Messungen wurden an Zinoberrot unter a) isothermen und b) dynamischen Bedingungen, in einem konstanten Stickstoffstrom durchgeführt. Die Ergebnisse wurden analysiert um die Zersetzungskinetik zu ermitteln und die Aktivierungsenergien zu berechnen. Im Falle der isothermen Zersetzung wurde gefolgert, daß die Diffusionsgeschwindigkeit der gasförmigen Produkte der steuernde Faktor ist, während bei der dynamischen Zersetzung die Keimbildung und das Wachstum innerhalb der Pb_3O_4-Teilchen von Bedeutung ist.

Резюме — С помощью ТГ проведены исследования красного свинца в изотермических и динамических условиях при постоянном токе азота. Проведен анализ результатов с целью установления кинетики разложения и энергии активации. В случае изотермического разложения установлено, что контролирующим фактором является скорость диффузии газообразных продуктов. В условиях динамического разложения важным является процесс образования зародышей в самих Pb_3O_4.