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KINETICS OF THERMAL DECOMPOSITION OF Co_3O_4 POWDER AND SINGLE CRYSTALS

The kinetic model

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The kinetics of the thermal decomposition of Co_3O_4 is described using a mixed-control model in which the reaction rate is controlled simultaneously by both a diffusional process and a chemical reaction. The observed dependence of the activation energy on the degree of decomposition, and the activation energies of the diffusion and of the chemical reaction are given.

The thermal decomposition of Co_3O_4: $Co_3O_4 \rightarrow 3CoO + 1/2O_2$ leads to the formation of a layer of CoO. This layer is very compact and well attached to the surface of the unreacted grain, as shown in our previous work [1].

In reference [1] we have shown that the kinetics of Co_3O_4 thermal decomposition under an oxygen partial pressure of 0.67 Pa can be described with very high accuracy by the following equation:

$$1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt^n \qquad (1)$$

where α is the degree of decomposition and k and n are constants.

The above equation has been derived directly from a kinetic analysis of the experimental α *vs.* t curves. We have shown that Eq. (1) can be regarded

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as a kinetic one, since it allows determination of an activation energy which actually depends on the degree of decomposition.

Equation (1) can be derived from the Ginstling-Brounstein model by assuming a phenomenological law of variation for the activation energy [3].

In the present paper we will show that it is also possible to describe our previous data on Co_3O_4 thermal decomposition in the scope of a mixed-control model. Such models have been developed by many authors [4, 5].

Results and discussion

Figures 1 and 2 show the kinetic curves $\alpha(t)$ obtained for Co_3O_4 thermal decomposition under an oxygen partial pressure of 0.67 Pa. The detailed description of the experiment is given in ref. [1] and [2]. Equation (1) was used to explain the experimental α vs. t curves in the scope of the extended Ginstling-Brounstein model [2, 3]. On the basis of this model, the observed dependence of the activation energy on α is given by

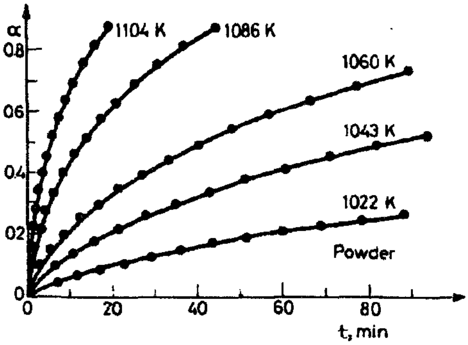

Fig. 1 α vs. time plots for thermal decomposition of Co_3O_4 powders

$$E(\alpha) = E_{0.5} + \frac{(1-n)RT}{n} \ln \frac{1-2\alpha/3-(1-\alpha)^{2/3}}{0.03671} \qquad (2)$$

where $E_{0.5}$ is the value of activation energy for $\alpha = 0.5$, n is the parameter defined in Eq. (1), T is the absolute temperature and R is the gas constant.

The numerical values of the activation energy decrease with α from 416 to 406 kJ/mole and from 475 to 453 kJ/mole for powders and single crystals, respectively. According to the assumptions of the extended Ginstling-Broumstein model, these values should represent the activation energy of diffusion as a rate-limiting step.

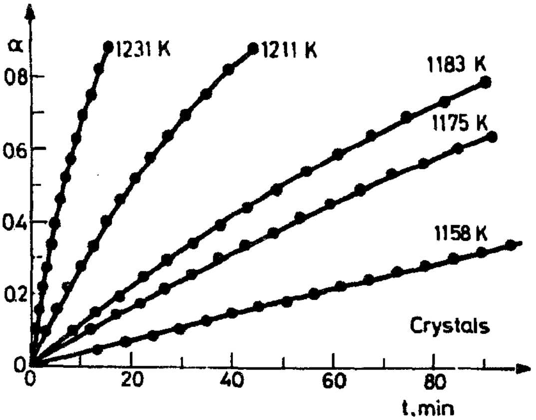

Fig. 2 α vs. time plots for thermal decomposition of Co_3O_4 single crystals

The interpretation proposed above to explain the experimental results on Co_3O_4 thermal decomposition may be disputed. First of all, the values obtained for the activation energy are much higher than those for any other known diffusional processes. Secondly, during the experimental work on Co_3O_4 thermal decomposition we noticed that the external oxygen pressure strongly influences the reaction rate. Preliminary results suggest that the rate of Co_3O_4 thermal decomposition changes in proportion to (p_r-p_o), where p_r is the equilibrium external oxygen pressure at a given temperature and p_o is the external oxygen pressure. This could indicate that the rate-limiting step is a chemical reaction. However, such a conclusion does not explain the changes in activation energy with the decomposition rate noted in many papers [1, 6-8]. Furthermore, our attempts to apply a simple reaction model to Co_3O_4 thermal decomposition were unsuccessful.

Taking the above considerations into account, we started with the hypothesis that Co_3O_4 thermal decomposition proceeds in the mixed-control region where both diffusional and chemical processes control the reaction simultaneously.

In the kinetic model presented below, the following assumptions are made:

1. the reaction proceeds in a spherical grain;

2. a layer of a solid product is formed on the surface of the unreacted grain during the reaction;
3. the chemical reaction is a first-order one;
4. the rate of diffusion of the gaseous product through the layer is comparable with the rate of the chemical reaction.

On the basis of the above assumptions, the following kinetic equation can be derived:

$$1-2\alpha/3-(1-\alpha)^{2/3}+s[1-(1-\alpha)^{1/3}]=k_r t \qquad (4)$$

Constants s and k_r are given by

$$s=\frac{2D}{R_0 k} \qquad\qquad k_r=\frac{2v_m D\,\Delta p}{R_0^2}$$

where D is the diffusion coefficient,
v_m is the molar volume of the substrate,
Δ_p is the difference between the equilibrium partial pressure of oxygen and the external pressure of oxygen,
k is the reaction rate constant, and
R_0 is the radius of a grain.

Equation (4) describes the $\alpha(t)$ curves of Co_3O_4 thermal decomposition with very high accuracy for α values in the range 0.1-0.85 for powder, and in the range 0.15-0.8 for single crystals. The standard deviation for the $|\alpha_{calc}-\alpha_{exp}|$ values is less then 0.007.

Table 1 Parameters s and k_r for thermal decomposition of Co_3O_4 powders

T (k)	s	$k_r x10^4$	r
1022	0.289	4.149	0.9993
1043	0.245	11.14	0.9993
1060	0.184	19.10	0.9993
1086	0..128	50.94	0.9996
1104	0.095	110.5	0.9996

Tables 1 and 2 contain calculated values of parameters s and k_r and regression coefficients r for various temperatures of decomposition of powders and single crystals, respectively.

Table 2 Parameters s and k_r for thermal decomposition of Co_3O_4 single crystalls

T (k)	s	$k_r x10^4$	r
1158	1.10	2.397	0.9957
1175	0.760	3.875	0.9951
1183	0.692	4.773	0.9953
1211	0.521	9.406	0.9952
1231	0.403	23.36	0.9952

We will now show that in the mixed-control kinetic model the observed activation energy depends on the degree of decomposition.

The observed activation energy can be defined by an expression having the form an Arrhenius law:

$$\frac{\delta}{\delta T}\ln\frac{\delta\alpha(t,T)}{\delta t}=\frac{E(\alpha,T)}{RT^2} \tag{5}$$

When $E(\alpha, T)$ does not depend on the degree of decomposition and on temperature, its value E_0 corresponds to the activation energy of the single rate-limiting process. If this condition is not satisfied $E(\alpha, T)$ will be an energetical parameter called the observed or apparent energy of activation. This parameter determines the differential increment of the logarithm of the reaction rate α for an increment of temperature δT.

Differentiating Eq. (4) leads to

$$\frac{d\alpha}{dt}=\frac{3v_m kD\Delta p(1-\alpha)^{2/3}}{kR_0^2(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]+DR_0} \tag{6}$$

Introducing Eq. (6) into (5) gives the following expression for $E(\alpha, T)$:

$$E(\alpha,T)=\frac{RT^2D\dfrac{d\ln k}{dT}+R_0kf_1f_2RT^2\dfrac{d\ln D}{dT}}{kR_0f_1f_2+D}+RT^2\frac{d\ln\Delta p}{dT} \tag{7}$$

where

$$f_1=(1-\alpha)^{1/3}$$

$$f_2 = (1 - f_1)$$

As the experimental data were obtained for an external oxygen pressure of ca. 0.67 Pa, we may take $p_o = 0$ and $\Delta_p = p_r$.
The temperature-dependence of the equilibrium partial pressure p_r is given by

$$p_r = p_r^o \, e^{\Delta H/R T}$$

where ΔH is the enthalpy change of the reaction. Assuming that the chemical reaction and diffusion are activated processes, the respective activation energies E_r and E_d are given by

$$E_r = R\,T^2 \,\frac{\mathrm{d}\ln k}{\mathrm{d}T} \tag{8}$$

$$E_d = R\,T^2 \,\frac{\mathrm{d}\ln D}{\mathrm{d}T} \tag{9}$$

Taking the above expressions into account, Eq. 7 leads to the following relation between the observed activation energy and the degree of decomposition:

$$E(\alpha, T) = \frac{D\,E_r + R^o k f_1 f_2 E_d}{k R_o f_1 f_2 + D} - \Delta H \tag{10}$$

Figure 3 gives the variation of the observed activation energy as a function of the degree of the decomposition for Co_3O_4 powder and single crystals.

For an evaluation of E_r and E_d, we use the values obtained for parameters s and k_r, which are related to E_r and E_d by

$$k_r = k_r^o \exp\left[-\frac{E_d - \Delta H}{R T}\right] \tag{11}$$

$$s = s_o \exp\left[\frac{E_r - E_d}{R T}\right] \tag{12}$$

where k_r^o and s_o are constants.

The slope of the straight line ln k_r *vs.*T^{-1} allows determination of the value of (E_d - ΔH), while the slope of the straight line ln s *vs.*T^{-1} gives the value of (E_r - E_d). In order to calculate E_r and E_d from the results presented, above we use the value of ΔH given in ref. [9] (ΔH = -342.2 kJ/mole).

This procedure leads to the following values:
for Co_3O_4 powder

E_d = 22.8 kJ/mole E_r = 153.0 kJ/mole
for Co_3O_4 single crystals

E_d = 11.8 kJ/mol E_r = 164.0 kJ/mole.

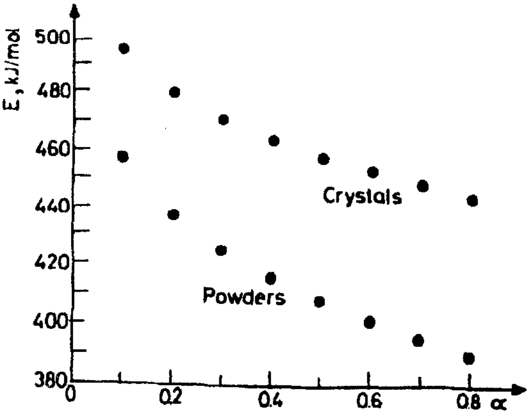

Fig. 3 Observed activation energy vs. *α* for Co_3O_4 powders and single crystals

It should be pointed out that, in the scope of the mixed-control kinetic model proposed above, previously determined high values of the apparent activation energy result from the presence of ΔH in Eq. (10). We could say, roughly speaking, that the apparent activation energy results from the addition of ΔH to the activation energy of the microscopic process. In contrast, the E_r and E_d values calculated in the present work do not include the value of ΔH.

As expected, the E_r values obtained from powder data and from single crystal data are very close. In contrast, powders exhibit an activation energy E_d for diffusion twice as high as that found for single crystals. This apparent discrepancy could originate in a large difference in the concentration of defects of various kinds, such as dislocations, cracks, etc. Actually, such a defect concentration partly related to mechanical strength is expected to be higher in a relatively large single crystal than in the very small crystals of a powder sample.

In conclusion, taking all these considerations into account, we may state that the activation energy values of Co_3O_4 thermal decomposition determined in the previous papers cannot be correct and that, in the investigated temperature range, the kinetics is controlled by both chemical reaction and diffusional processes, for which the respective activation energies have been determined.

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Zusammenfassung - Es wurde die Kinetic der thermischen Zersetzung von Co_3O_4 mittels eines Modelles beschrieben, bei dem die Reaktionsgeschwindigkeit sowohl durch Diffusionsvorgänge als auch durch chemische Reaktionen beeinflut wird. Die gefundene Abhängigkeit der Aktivierungsenergie vom Grad der Zersetzung, von Diffusion und chemischer Reaktion wird gegeben.