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ON THE THERMAL DECOMPOSITION OF K_2PtCl_4 IN A HYDROGEN ATMOSPHERE

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ABSTRACT

The reaction of single crystals and powders of K_2PtCl_4 with hydrogen is studied by means of thermogravimetry (TG) at temperatures between 175 and 225°C and by optical microscopy. Two different mechanisms are observed. The rate of decomposition of single crystals is determined by the displacement of the reaction interface, which is similar in every crystallographic direction.

The rate of decomposition of the powders is limited by the rate of nucleation in the powder particles. For both mechanisms the kinetic parameters are calculated. The activation energy for the displacement of the interface is much higher than the one necessary for nucleation.

1. INTRODUCTION

Single crystals of K_2PtCl_4 and K_2PdCl_4 were decomposed in a hydrogen atmosphere according to the reaction

$$K_2MCl_4 + H_2 \rightarrow 2KCl + M + 2HCl\uparrow \qquad (1)$$

$$M = Pt \text{ or } Pd$$

It appeared that for both compounds the orientation relationships between single crystals and their decomposition products were different[1].

Because in both cases the crystal structures are similar (the lattice parameters are the same within a few hundredths of an Ångstrom) it is not possible to base an explanation for their different behaviour on geometrical variations. However, the difference could be caused by an unlike kinetic behaviour of the decomposition of both salts.

In this paper the mechanism of the reaction of single crystals and powders of K_2PtCl_4 with hydrogen will be dealt with. The decomposition of K_2PdCl_4 is still being studied.

2. EXPERIMENTAL PART

2.1. *Preparation of single crystals and powders of K_2PtCl_4*

The single crystals were grown by slow evaporation of a saturated solution at 25°C (ref. 1). These crystals were bounded by four rather perfectly shaped {100} prism faces, mutually perpendicular and parallel to the tetragonal C-axis, and by two (001) basal faces perpendicular to the C-axis. Although the length direction of the crystals always ran parallel to the C-axis, the ratios of the dimensions were quite different for each of them (Table 1).

The powders, delivered by Drijfhout (Amsterdam) and prepared from KCl and $PtCl_2$ in acid solution, were reagent grade. The diameter of the particles ranged from 1–50 μm.

TABLE 1

SINGLE CRYSTALS OF K_2PtCl_4

Sample number	*Dimensions*			*Initial weight (mg)*	*Weight loss*[a] *observed* (%)
	a (*mm*)	*b* (*mm*)	*c* (*mm*)		
C_1	2.010	2.104	3.982	57.52	17.7
C_2	1.862	1.935	4.131	46.81	17.4
C_3	0.824	1.067	3.985	10.93	17.2
C_4	1.326	1.369	7.900	48.39	17.5

[a] The theoretical weight loss = 17.08%.

2.2. *Thermogravimetry*

For both single crystals and powders the weight loss of the decomposition reaction was measured by thermogravimetry. Therefore a symmetrical thermobalance was used as described elsewhere[2,3].

Both sample and reference holders were cylindrical alumina crucibles covered with platinum lids. The diameter of the crucibles was about 10 mm and their height about 3 mm. Before an experiment was started all the air in the balance was removed by evacuation. After passing a stream of high purity nitrogen the heating and the decomposition were carried out in a stream of high purity hydrogen (30 ml per minute). Because the thermobalance is designed symmetrically, evacuation of the balance or change in the kind of gas used had little or no influence on the position of the baseline.

In case of isothermal decomposition experiments the reaction temperature was reached at a heating rate of 1.2 or 2.4 degrees per minute.

There was a good agreement between the measured and the calculated weight losses (Tables 1 and 2). The small differences are most likely caused by the loss of water included in the samples.

TABLE 2

DECOMPOSITION OF POWDERS OF K_2PtCl_4

Variation of the rate constants k_N, calculated according to the A.E. eqn (13) for $n = n$ and $n = 1$, with the temperature T.

Sample number	*T* (°C)	*n*	k_N (min^{-1})		*Weight loss*[a] *observed* (%)
			$n = n$	$n = 1$	
P_1	175.5	1.047	$9.68 \cdot 10^{-3}$	$10.18 \cdot 10^{-3}$	17.2
P_2	178.5	1.098	$10.75 \cdot 10^{-3}$	$11.91 \cdot 10^{-3}$	17.4
P_3	180.2	1.021	$11.30 \cdot 10^{-3}$	$11.55 \cdot 10^{-3}$	17.4
P_4	185.2	0.994	$13.64 \cdot 10^{-3}$	$13.54 \cdot 10^{-3}$	17.5
P_5	186.3	1.014	$14.09 \cdot 10^{-3}$	$14.35 \cdot 10^{-3}$	17.4
P_6	191.0	0.966	$19.76 \cdot 10^{-3}$	$18.97 \cdot 10^{-3}$	17.4
P_7	194.9	1.013	$21.37 \cdot 10^{-3}$	$21.75 \cdot 10^{-3}$	17.5

[a] The theoretical weight loss at the decomposition is 17.08%.

2.3. *Preparation of the samples for optical microscopy*

For microscopic examination the partly decomposed single crystals were embedded in a two-components synthetic resin with either a {100} or a (001) crystallographic plane parallel to the specimen surface.

After hardening the specimen was polished to expose the decomposition process inside the crystal by dark field microscopy. During the hardening process of the resin the decomposed layer becomes slightly crushed.

3. DECOMPOSITION OF THE SINGLE CRYSTALS

Most decomposition processes are ruled by one or more of the following reaction steps: (1) nucleation; (2) growth of the nuclei; (3) diffusion of the reaction products to and from the reaction interface.

In this case the diffusion of H_2 and HCl through the product layer can be neglected. According to the reaction equation, the decrease in volume of the solid state is about 32%. Because the shape of the specimens remains practically unchanged during decomposition, the porosity must be so great, that gaseous products can diffuse freely to and from the interface[4]. Thus only the first two steps are left.

When single crystals are gradually heated in hydrogen, black needles often arise at temperatures of about 110°C at the surface or even inside the matrix of the crystals[1]. These thin needles, lying parallel to a ⟨100⟩ direction, are most likely developed along edge dislocations. Their formation can only be revealed under a microscope (magnification 60×) and cannot be detected by thermogravimetry. On further heating the decomposition starts over the whole surface.

From this last observation and from the microscopic observations of cross-sections of decomposed single crystals embedded in resin, the following conclusions may be drawn:

(i) Almost immediately after the decomposition is started the whole crystal surface is covered with a closed layer of decomposed products. A nucleus apparently has the tendency to spread very rapidly along the crystal surface, once it is formed.

The rate of progress of the interface inside the matrix, this means the growth rate of the nuclei perpendicular to the crystal surface, is a lot smaller and therefore determines the rate of the decomposition process.

(ii) The shape of the reaction interface remains similar to that of the single crystal to a degree of decomposition depending on the quality of the crystal (Figs. 1 and 2).

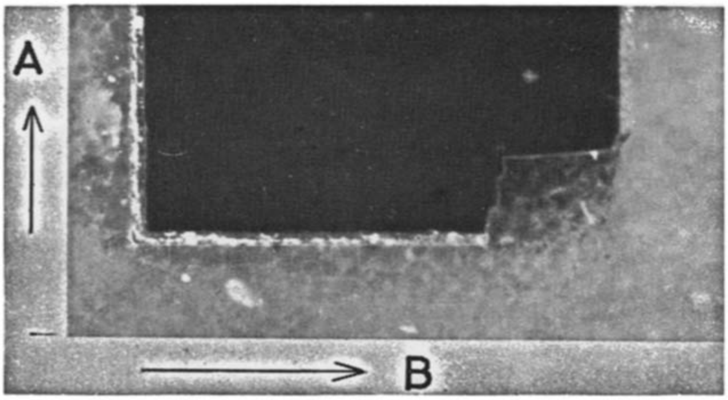

Fig. 1. Cross-section of a partly decomposed tetragonal single crystal of K_2PtCl_4 with a (001) plane parallel to the surface.

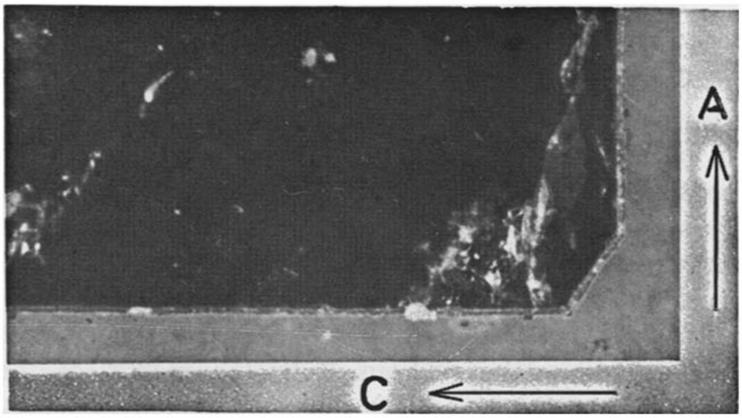

Fig. 2. Cross-section of a partly decomposed tetragonal single crystal of K_2PtCl_4 with a {100} plane parallel to the surface.

(iii) These figures show that the thickness of the decomposed layer is the same in all three crystallographic main directions A, B and C. So the rate of displacement of the interface is about the same in every crystallographic direction.

(iv) The angles in the interface at the edges of the crystal are not rounded during the displacement. This confirms the conclusion that the diffusion is not rate determining.

3.1. Calculation of the growth rate k_G

An isotropic decomposition reaction is considered, starting at the crystal surface with an interface, which proceeds at isothermal conditions into the matrix of the crystal with a constant growth rate k_G.

The next formulas can be deduced:

$$\alpha = (G_0 - G_t)/(G_0 - G_\infty) \tag{2}$$

$$1 - \alpha = V_t/V_0 = (a - 2\delta)(b - 2\delta)(c - 2\delta)/abc \tag{3}$$

$$\alpha = 2\delta(1/a + 1/b + 1/c) - 4\delta^2(1/ab + 1/bc + 1/ac) + 8\delta^3/abc) \tag{4}$$

$$k_G = \mathrm{d}\delta/\mathrm{d}t \tag{5}$$

This gives

$$\delta = k_G(t - t_0) \tag{6}$$

$$\mathrm{d}\alpha/\mathrm{d}t = k_G\{2(1/a + 1/b + 1/c) - 8\delta(1/ab + 1/bc + 1/ac) + 24\delta^2/abc\} \tag{7}$$

with:

a, b, c*	dimensions of the single crystal at $t = t_0$
δ	thickness of the decomposed layer
V_0	abc
V_t	volume of undecomposed material at $t = t$
G_0	weight at $t = t_0$
G_t	weight at $t = t$
G_∞	weight after completion of the reaction
α	degree of progress of the reaction
t_0	time of the beginning of the isothermal reaction at $\alpha = 0$.

To determine k_G two kinds of thermogravimetric experiments were carried out.

(i) A number of single crystals was completely decomposed isothermally at temperatures between 189 and 220°C after a heating period. Unfortunately most crystals developed large cracks during decomposition or even during the heating. This happened especially at higher temperatures.

Less perfect crystals for example those containing inclusions, as could be seen under a microscope, gave more rise to cracks than the more perfect ones. These cracks were attended with the appearence of jumps in the weight-change curves. The curves obtained for such crystals were partially or totally useless, because after the existence of a crack the reaction interface was indefinable.

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*These dimensions a, b, c must not be confused with those of the unit cell of the lattice.

Only three crystals showed smooth curves during the heating period and could be decomposed under isothermic conditions to a certain degree before cracks arose (Table 3). For these crystals the thickness δ of the decomposed layer was calculated from α by means of eqn (4) and plotted as a function of the reaction time in Fig. 3. In this figure the curve belonging to crystal C_3, decomposed at 219.5°C, shows a deviation of the slope at $\delta = 0.055$ mm. This deviation was caused by the development of a crack, resulting in an increased reaction rate. From this point at $\alpha = 0.25$ the curve is useless. From the slope of the curves the growth rate k_G can be calculated according to eqn (5) (Table 3).

(ii) Some crystals were decomposed stepwise, every step corresponding with a certain reaction temperature. Only two crystals could be used, one starting from

TABLE 3

ISOTHERMAL DECOMPOSITION OF SINGLE CRYSTALS OF K_2PtCl_4

The growth rate k_G as a function of the temperature T.

Sample number	*T* (°*C*)	k_G (*mm min*$^{-1}$)
C_1[a]	189.2	$1.96 \cdot 10^{-4}$
C_2	199.8	$5.06 \cdot 10^{-4}$
C_3	219.5	$15.7 \cdot 10^{-4}$

[a] This sample is also used for step-wise decomposition (Table 4).

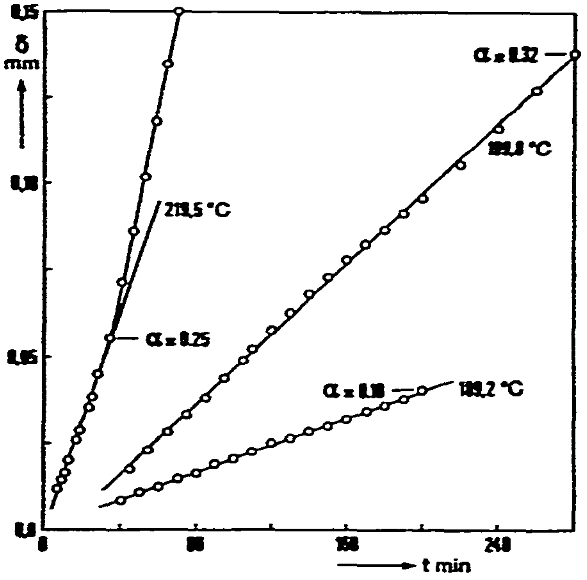

Fig. 3. Isothermal decomposition of single crystals of K_2PtCl_4. The thickness δ of the decomposed layer is plotted against the time t. The line through the observed values of δ at 199.8°C remained straight till $\alpha = 0.70$. O, observed values; —, calculated values.

TABLE 4

STEP-WISE DECOMPOSITION OF SINGLE CRYSTALS OF K_2PtCl_4
The growth rate k_G as a function of the temperature T.

Sample number C_1			*Sample number C_4*		
Step number	*T (°C)*	*k_G (mm min^{-1})*	*Step[a] number*	*T (°C)*	*k_G (mm min^{-1})*
7	163.8	$0.41 \cdot 10^{-4}$	2	189.5	$2.10 \cdot 10^{-4}$
5	182.6	$1.23 \cdot 10^{-4}$	1	190.8	$2.73 \cdot 10^{-4}$
1	189.3	$1.90 \cdot 10^{-4}$	11	191.0	$2.24 \cdot 10^{-4}$
6	189.3	$1.93 \cdot 10^{-4}$	3	195.8	$3.34 \cdot 10^{-4}$
8	189.3	$1.90 \cdot 10^{-4}$	4	200.2	$5.02 \cdot 10^{-4}$
9	189.3	$1.80 \cdot 10^{-4}$	10	200.2	$4.00 \cdot 10^{-4}$
11	189.3	$2.00 \cdot 10^{-4}$	5	205.0	$6.99 \cdot 10^{-4}$
2	190.2	$1.85 \cdot 10^{-4}$	6	210.0	$8.92 \cdot 10^{-4}$
3	198.1	$3.04 \cdot 10^{-4}$	7	214.6	$12.47 \cdot 10^{-4}$
4	212.2	$9.64 \cdot 10^{-4}$	8	218.5	$15.94 \cdot 10^{-4}$
10	222.8	$25.50 \cdot 10^{-4}$	9	222.5	$27.10 \cdot 10^{-4}$

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[a] The step numbers correspond with their sequence in the decomposition process. Especially with sample number C_1 the reproducibility of the process was checked by returning several times to the same reaction temperature $T = 189.3$ °C.

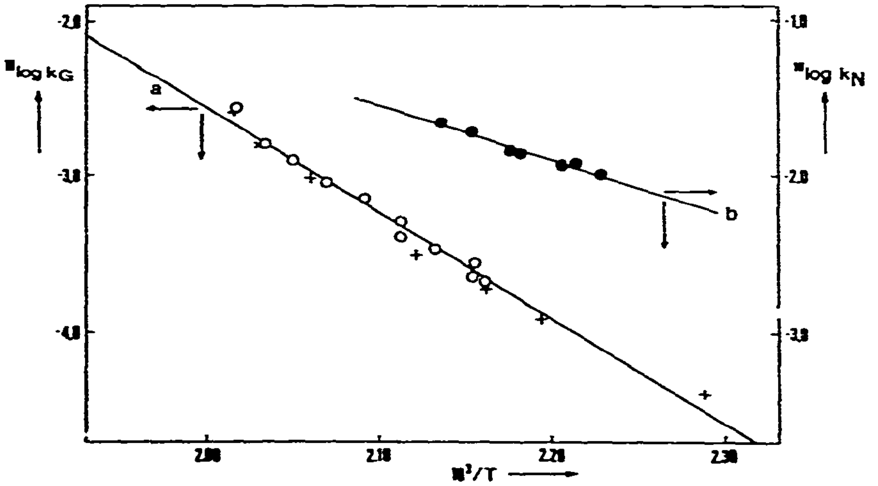

Fig. 4. Decomposition of K_2PtCl_4. Arrhenius plot of the rate constants k_G (a) and k_N (b) for the decomposition of single crystals and powders, respectively. —, calculated values; ○ +, observed values for the stepwise decomposition of single crystals; ×, observed values for the isothermal decomposition of single crystals; ●, observed values for the isothermal decomposition of powders. k_G (mm min^{-1}), k_N (min^{-1}), and T (K).

10 percent of decomposition, because before this percentage the above-described isothermal method was applied (sample number C_1).

In this stepwise decomposition method the slope of the weight change curve is about constant in one step, because in one single step only a small fraction is decomposed. From this slope the value of $d\alpha/dt$ can be derived.

From eqn (4) the average value of δ for every step can be calculated and subsequently with eqn (7) the growth rate k_G (Table 4). There is a good agreement between the k_G values of both kinds of experiments. In Fig. 4 the k_G values are plotted in an Arrhenius plot. From

$$k_G = k_G^0 \exp(-E_G/RT) \tag{8}$$

it follows that

$$\log k_G^0 = 10.91 \pm 0.46$$

$$k_G^0 = 8.2 \cdot 10^{10} \text{ mm min}^{-1}$$

and the energy of activation

$$E_G = 30.8 \pm 1.0 \text{ kcal mol}^{-1}$$

4. DECOMPOSITION OF THE POWDERS

The powders showed a decomposition behaviour quite different from that of single crystals. Powders with an average weight of 11 mg were isothermally decomposed in a constant stream of hydrogen at temperatures ranging from 175 to195 °C. The degree of progress of the reaction was measured by TG as a function of time t (Fig. 5).

The results were compared with many equations[5,6] including those based on diffusion-controlled processes. It appeared that the decomposition can be described most adequately by the Avrami–Erofeev equation[3-5]:

$$-\ln(1-\alpha) = k(t-t_0)^n \tag{9}$$

For the powders the value $n = 1$ appeared to fit very closely (Fig. 6).

Such a first order reaction can be obtained by two totally different reaction mechanisms:

(i) One mechanism is based on a very fast nucleation process followed by a rather slow development of the nuclei in only one crystallographic direction[3,6].

(ii) Another mechanism includes a slow nucleation process followed by a rather fast decomposition of the powder particle once holding a nucleus[7].

Microscopic observations of partly decomposed powders reveal the existence of totally decomposed particles next to particles which show no decomposition at all. This points to the second mechanism and is inconsistent with the first one. Furthermore at the decomposition of single crystals no preference was observed for one single direction. This also testifies against the first mechanism. The second mechanism only

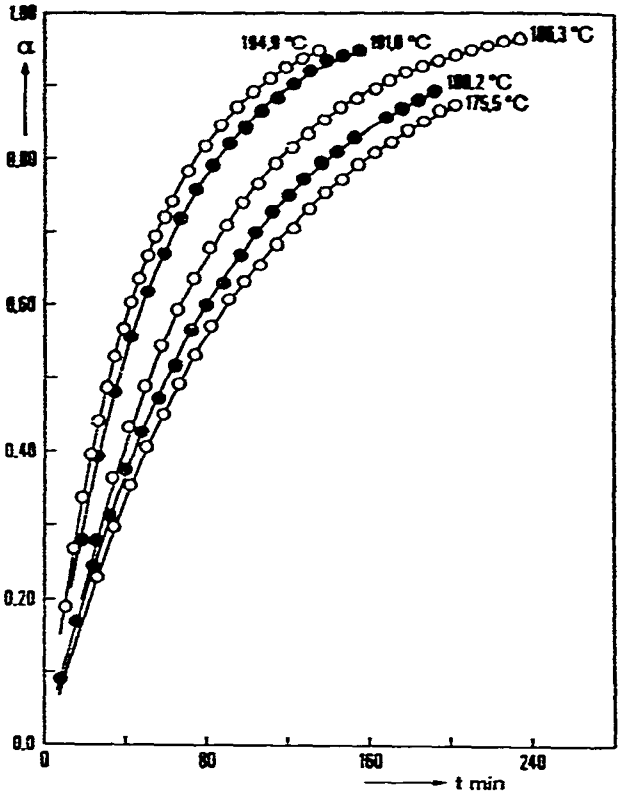

Fig. 5. Decomposition of powders of K_2PtCl_4. The degree of decomposition is plotted against the time t. ○ ●, observed values; —, values calculated according to a first order reaction mechanism. The samples P_2 and P_4 at 178.5 and 185.2 °C are omitted for the sake of clearness.

leads to an exact first order mechanism if every powder particle has exactly the same chance k_N to start with the decomposition reaction. The decomposition of a particle begins at the moment that a potential nucleus is transformed into a growth nucleus. So:

$$dN/dt = k_N(N_0 - N) \tag{10}$$

N_0 = number of powder particles at time $t = t_0$

N = number of powder particles at time $t = t$ holding a growth nucleus; this corresponds with the number of decomposing or already decomposed particles

k_N = chance that a powder particle starts to decompose, which corresponds with the rate of nucleation.

This gives:

$$-\ln (N_0 - N)/N_0 = k_N t \tag{11}$$

$$-\ln (1 - \alpha) = k_N t \tag{12}$$

So this mechanism corresponds with a first order reaction. In the experiments

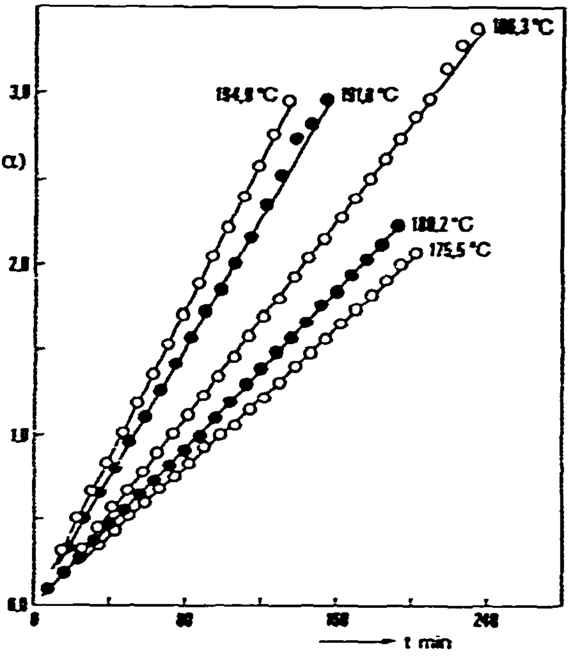

Fig. 6. Decomposition of powders of K_2PtCl_4. Elaboration of the data in accordance with first order reaction kinetics. ○ ●, observed values; —, calculated values. The samples P_2 and P_4 at 178.5 and 185.2 °C are omitted for the sake of clearness.

deviations from the exact first order reaction will arise, since the chance to start with the reaction is not the same for every particle, caused by differences in particle size, ranging from 1 to 50 μm, and because the time needed by the larger particles to decompose after nucleation cannot be completely neglected.

Nevertheless the influence of differences in particle size is only small as appears from the next calculation. Let us take for example a spherical particle with a diameter of 10 μm. With the growth rate found for single crystals at a temperature of 185.2 °C a half lifetime of 6 min can be calculated, while the half lifetime of the first order reaction at this temperature is 48 min. Furthermore from experiments with single crystals it follows that a considerable number of larger powder particles will burst during the reaction and therefore decompose much faster than would be expected from their size at time $t = 0$. It was also visible under a microscope that after decomposition no large particles were left.

4.1. Calculation of the kinetic parameters

Starting from the formula

$$-\ln(1-\alpha) = k_N(t-t_0)^n \qquad (13)$$

the values of k_N for $n = n$ and $n = 1$ are calculated and reported in Table 2. From $\log k_N$ plotted against $1/T$ for $n = 1$ (Fig. 4), the values of the pre-exponential factor k_N^0 and the energy of activation E_N can be derived.

$$k_N = k_N^0 \exp(-E_N/RT) \tag{14}$$

$$\log k_N^0 = 5.87 \pm 0.69$$

$$k_N^0 = 7.5 \cdot 10^5 \text{ min}^{-1}$$

$$E_N = 16.2 \pm 1.4 \text{ kcal mol}^{-1}$$

CONCLUSIONS

(i) The rate of decomposition of the single crystals is governed by the chemical reaction on the interface and so by the rate of displacement of the interface k_G, which is similar in every crystallographic direction.

Even if the reaction rate in the direction of the C-axis differs a little from those in the A- or B-directions, this difference does not have much influence on the calculated value of the decomposition rate, because a (001) plane is far smaller than a $\{100\}$ plane.

(ii) The rate of decomposition of the powders is regulated by the nucleation rate k_N.

(iii) The reason for the difference in behaviour is the fact, that the powders are composed of a lot of very small particles, which will decompose relatively fast once the decomposition is started, while the single crystals are so large, that the rate of displacement of the interface is slow compared with the nucleation rate at the surface.

(iv) Because in this special case both nucleation and growth can be studied almost completely separated, it is possible to determine the kinetic parameters for both processes individually.

(v) The value of the activation energy for the displacement of the interface E_G is much higher than the one necessary for nucleation E_N.

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