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The Influence of Experimental Conditions on the Size and Shape of Crystallites Produced by a Solid State Reaction. Case of $Cd(OH)_2$ Decomposition into CdO

P. DUMAS, N. EA, J. C. NIEPCE, AND G. WATELLE

Laboratoire de Recherche sur la Réactivité des Solides, Faculté des Sciences Mirande, Campus Universitaire, 21000 Dijon (France)

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The results reported were obtained during investigation of the ideal experimental conditions for study of the structural transformation mechanism which occurs in the decomposition reaction of $Cd(OH)_2$ into CdO. By measuring the sizes of CdO crystallites produced as a function of experimental conditions in which decomposition is carried out, it has been possible to distinguish pressure–temperature domains in which CdO formation occurs alone from other domains in which formation is always associated with evolution phenomena.

A particular influence of water vapor is reported. The results are discussed in relation to the reaction mechanism.

A very easy method using X-ray diffraction peak measurements has been used for crystallite shape characterization.

I. Introduction

The study of a solid state reaction mechanism is usually approached either through kinetic investigations (*1, 2*) or observations under optical or electron microscopy (*3, 4, 5*). When looking for the features allowing the transformation modes to be distinguished in solids, the transformation mode is noticed to have a prevailing importance on the division state of the solid obtained. Indeed, if we deal with a "germination-growth" mode the following features must be put in evidence. The crystallite sizes of the solid obtained must increase with the extent of reaction and decrease as the transformation rate increases under the influence of a temperature variation. Those sizes are not limited *a priori*; operating cautiously bigger crystals can be obtained. Alternatively, when dealing with a transformation mode without diffusion, e.g. a "shear transformation," the crystallite sizes of the solid obtained must be constant throughout reaction and have the same value whatever the transformation temperature. Those dimensions are limited to maximum values depending on the solids. The resulting crystallite shape is related only to the orientation symmetry group of the crystalline solid produced in a "germination-growth" mode whereas it is also dependent on the symmetry group of the precursor in the case of a shear transformation.

These reflections show the importance of the information which can be obtained by a study of the division state of the solid produced through a solid state reaction. The search of the structural transformation mechanism by studying the division state was

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undertaken for a well-known topotactic reaction which had been interpreted in terms of germination and growth, i.e. the decomposition of magnesium (*6*, *7*) and cadmium hydroxides (*8*).

However, to validate such a study, the dimensions and shape of the resulting crystallites must only depend on the transformation mode, i.e. no other phenomenon such as sintering for instance must involve any dimension change in the crystallites after formation. It was thus necessary to undertake a prior study to find out the experimental conditions in which these requirements would be fulfilled. A systematic study was made of the influence on the oxide division state of the experimental conditions under which this decomposition is carried out; the results are reported below.

All the results reported were obtained by classical powder X-ray diffraction with step scanning device and by easy crystallite size calculations from half-peak breadth measurements. An easy method was used for crystallite shape characterization from these measurements although, it is well known, the shape determination is quite impossible from the same measurements (*9*, *10*).

II. Experimental

II-1. Decomposition Conditions

A cadmium hydroxide (Prolabo) with large crystallite sizes was used: mean thickness perpendicular to $(001) \simeq 680$ Å and mean diameter perpendicular to $(100) \simeq 3500$ Å. The decomposition reaction was carried out in a thermobalance in which the experimental conditions were easily controlled: sample weight q, temperature T and vacuum or water-vapor pressure P. This has been previously described (*11*). We only want to give more accurate information about time, t, and sample weight, q.

Preservation of the Experimental Conditions: t (Time of Heating at Decomposition Temperature)

This time t is indifferently called in the text "heating time" or "decomposition time." t is the time between the setting of the decomposition temperature on the programmator and the end of heating. Figure 1 shows that heating and cooling are not instantaneous. About 25 min are required to reach the isothermal conditions under vacuum but only two or three under water-vapor pressure; cooling is slower. Thus a minimum value of this time is imposed by the apparatus and the residual pressure.

Weight of Sample Used for Each Decomposition: q

For each experiment 11 mg of $Cd(OH)_2$ were well sprinkled over a platinum crucible (diameter: 15 mm). In such conditions there is no influence of powder thickness. We effected some decompositions using 200 or 300 mg; especially under vacuum the results are distorted by the existence of a water-vapor pressure in the powder layer during decomposition (*12*). This phenomenon was also discussed by P. J. Anderson *et al.* (*7*).

II-2. X-ray Procedures and CdO Powder Characterization

Pure CdO can be kept without any difficulty in ordinary conditions of temperature and pressure. So it was possible to record the X-ray diffraction peaks of each

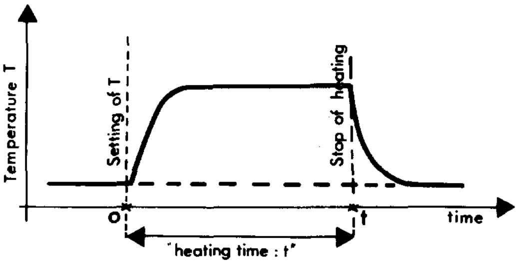

FIG. 1. Temperature curve during the preparation of a CdO sample.

sample after preparation in the thermobalance without a special apparatus. The conditions were as follows:

Siemens Kristalloflex IV Generator,

Ni Filtered CuK_α radiation,

Siemens Goniometer (divergence slit = 1 mm; receiving slit: 0.05 mm for step scanning or 0.2 mm for continuous conditions; Soller slits = ±4°),

Step scanning conditions (0.02° 2θ/120 s) (results were plotted with a 160 mm/° 2θ scales),

Continuous conditions (goniometer 1° 2θ/8 min and recorder 20 mm min).

Comparative results were sufficient for this study and half-peak breadths $\Delta 2\theta_{hkl}$ had permitted the different samples to be classified in terms of their mean apparent sizes D_{hkl} without ambiguity. Mean size calculations were made with the Scherrer equation (*13*) after correction of the half widths by the Warren method (*14*). The instrumental broadening was obtained with a BDH sample of CdO sintered at 600°C for 36 hr.

Let us now consider the ratios of the half-peak breadths of a same diffractogram. In exceptional cases such as those of hexagonal crystallites of $Cd(OH)_2$ or $Mg(OH)_2$ these ratios give direct information on the crystallite shape. In a more general case it is not possible. Nevertheless these ratios are always a function of shape, even if the latter is unknown. Thus, calculation of these ratios could be a very easy means of characterization of the crystallite shape. For samples with a similar origin it is reasonable to think that these ratios would be constant if the shape is conserved; on the contrary they would vary if the crystallite shape is not the same. In this sense we shall give, for each sample, the values of the ratios k_1 and k_2 of the half-peak breadths of 111, 200 and 220 CdO diffraction peaks.

$$k_1 = \Delta 2\theta_{111}/\Delta 2\theta_{200}, \qquad k_2 = \Delta 2\theta_{111}/\Delta 2\theta_{220}.$$

III. Results

Temperature and water-vapor pressure within the reactor seemed to be the two main experimental parameters which can have an influence on the sizes and shape of the oxide crystallites produced by decomposition of the hydroxide. The following results give some information about the influence of these two parameters.

III-1. Influence of Temperature on Crystallites Sizes

Figures 2 and 3 exhibit a different influence of temperature according as the decomposition is carried out in a good vacuum with a very low residual water-vapor

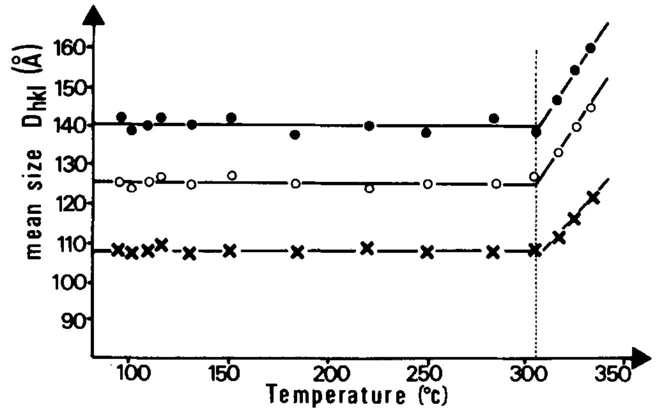

FIG. 2. Mean crystallite sizes D_{hkl} of oxides obtained at various temperatures, in vacuum (decomposition time = 18 hr): ● from 111 peak; ○ from 200 peak; × from 220 peak.

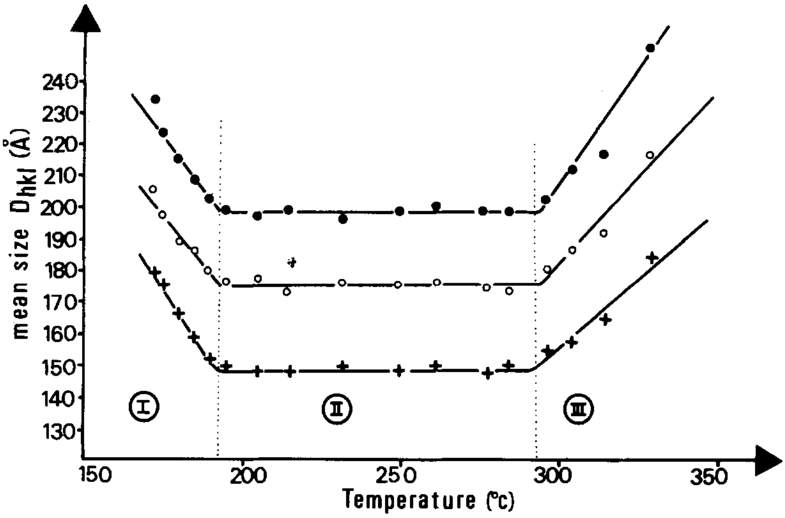

FIG. 3. Mean crystallite sizes D_{hkl} of oxides obtained at various temperatures, in water vapor (P_{H_2O} = 5 torr, decomposition time = 18 hr): ● from 111 peak; ○ from 200 peak; + from 220 peak.

pressure or, on the contrary, in a water-vapor atmosphere. These two figures give the variations, with oxide preparation temperature, of the mean crystallites sizes D_{hkl} calculated from the three main diffraction peaks of cadmium oxide, 111, 200 and 220. In both cases, whatever the temperature the heating time is 18 hr and the initial hydroxide sample weight is 11 mg.

One can observe two temperature ranges (Fig. 2) when decomposition occurs in vacuum. From the lower temperatures at which decomposition is possible, about 80°C up to 300°C, the mean crystallite sizes D_{hkl} are independent of T. Above 300°C, the higher the temperature T the larger the crystallite sizes D_{hkl}.

Figure 3, on the contrary, reveals three temperature ranges when decomposition is carried out under a water vapor atmosphere:

a range, termed I in Fig. 3, over which the higher the decomposition temperature the smaller the crystallite sizes;

a range, termed II, in which the sizes do not vary with temperature.

finally, a range III, in which an increase of temperature results in an increase in the crystallite sizes.

III-2. Influence of Water Vapor Pressure on Crystallite Sizes

Experiments similar to those which gave the curves in Figs. 2 and 3, have been reproduced under various water-vapor pressures P. Figure 4 shows the results obtained in the case of the mean crystallite size D_{111}, calculated from the broadening of the 111 peak; analogous curves represent the variation of the other crystallite sizes calculated from the other diffraction peaks.

All the $D = f(T)$ curves obtained for the various water-vapor pressures, equal to or higher than 1 torr, look like the curves in Fig. 3, i.e. they exhibit particularly the same three temperature ranges in which D varies differently with T. But the differences between the various curves reveal partially the influence of water vapor. When the pressure P is higher, the temperature range in which D does not vary with T is narrower, in the two other ranges the variations of D with T seem to be more rapid. Finally we can see that at a same temperature, the higher the pressure the larger the oxide crystallite size D obtained.

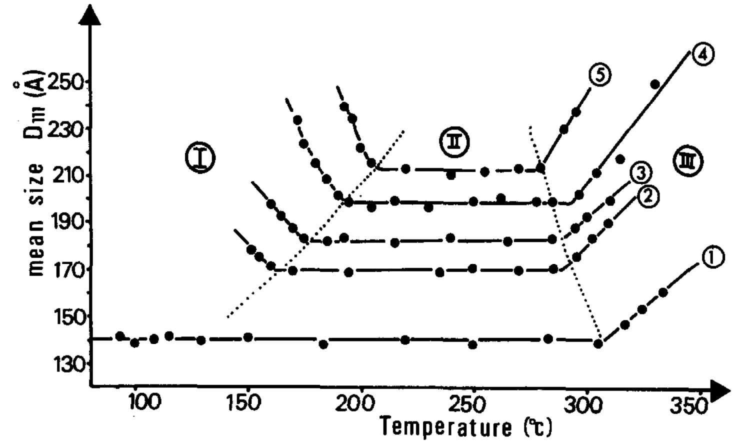

FIG. 4. Mean crystallite size D_{111} of oxides obtained at various temperatures, for several water-vapor pressures (decomposition time $t = 18$ hr): ① 5.10^{-5} torr; ② 1 torr; ③ 2 torr; ④ 5 torr; ⑤ 17.5 torr.

III-3. Influence of Experimental Conditions on Crystallite Shape

During such a study of the influence of experimental conditions on the division state of a solid produced by a solid state reaction it seems also interesting to obtain some information on crystallite shape. The crystallites are the elementary particles generated by the transformation. Their shape is related to the structural transformation mode thus any information on the shape is highly valuable.

It has been said that X-ray diffraction peak profile analysis often cannot define this shape but this technique is the only one able to give direct information on the shape. Indeed, the crystallite is the coherent diffraction domain, i.e. the domain of perfect continuity of the crystalline lattice; generally neither classical electron microscopy nor small angle X-ray scattering can exactly determine size and shape of the crystallites.

The experimental results reported in this paragraph bring a very easy characterization of the shape by means of half peak breadth measurements.

The k_1 and k_2 ratios calculated from the half-widths of the main diffraction peaks of the various sample used for obtaining the curves in Figs. 2, 3 and 4 are listed in Tables Ia, b and c. These ratios keep constant values, account taken of experimental errors, whatever the experimental errors.

The values listed in the upper part of Table Ia give the experimental error around the two values, $k_1 = 0.89$ and $k_2 = 0.72$ (*10*), obtained with crystallites of same sizes. The fluctuations of k_1 and k_2 around these two values are not larger in the other P, T ranges in which crystallite sizes are different. It is only in domain III (Fig. 4), and for sufficiently high temperatures, that variations of these ratios can be observed (for example, $k_1 = 0.931$ and $k_2 = 0.794$ at $T = 455°C$ and $P = 8$ torr).

When the sizes vary but not the ratios, this means that the crystallites remain homothetic one from the others. The crystallites produced by the decomposition reaction of $Cd(OH)_2$ have a very characteristic shape which is only changed by a higher temperature treatment. But at such a temperature, as we shall see in the next paragraph, phenomena subsequent to crystallite formation occur.

Several authors used totally different approaches to make this crystallite shape clearer; the results obtained are in agreement (*10, 15*).

TABLE I

k_1 AND k_2 RATIOS CHARACTERISTIC OF CRYSTALLITE SHAPE OF CdO PREPARED AT VARIOUS TEMPERATURES

(a) In vacuum

Temperature (°C)	k_1	k_2
94	0.88	0.72
100	0.89	0.72
109	0.89	0.72
115	0.89	0.72
130	0.89	0.72
150	0.89	0.72
183	0.90	0.73
220	0.89	0.73
250	0.90	0.73
283	0.88	0.72
305	0.91	0.73
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317	0.90	0.72
325	0.91	0.71
333	0.89	0.71

(b) In water-vapor pressure, $P = 5$ torr

Temperature (°C)	k_1	k_2
172	0.89	0.73
175	0.91	0.73
180	0.89	0.72
185	0.90	0.72
190	0.90	0.72
- - - - -	- - - - -	- - - - -
195	0.89	0.71
205	0.90	0.71
215	0.88	0.70
232	0.90	0.72
250	0.89	0.71
262	0.89	0.71
278	0.89	0.70
285	0.88	0.71
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297	0.90	0.72
305	0.89	0.71
315	0.89	0.71
330	0.89	0.71

The dashed lines in (a) and (b) correspond to the dotted lines in Figs. 2 and 3.

(c) Mean values of k_1 and k_2, under several water-vapor pressures, in the different temperature ranges of Fig. 4

Temperature (°C)	Ratios	Water-vapor pressures (Torr)				
		2.10^{-4}	1	2	5	17.5
[a]	k_1		0.91	0.89	0.89	0.91
	k_2		0.73	0.73	0.72	0.71
240	k_1	0.90	0.89	0.88	0.89	0.91
	k_2	0.72	0.73	0.72	0.71	0.73
340	k_1	0.90	0.90	0.90	0.90	0.89
	k_2	0.71	0.73	0.73	0.72	0.70

[a] 155°C (1 torr), 165°C (2 torr), 180°C (5 torr), 196°C (17.5 torr).

IV. Discussion and Further Results

The experimental results which have already been reported, show that the experimental conditions in which the decomposition is carried out have a great influence on the division state of the oxide produced. We will try now to distinguish, experimentally, the conditions in which crystallite formation is always associated with side effects from those in which crystallite size is only related to the formation processes. For this reason we will now study what happens in the three various ranges of temperature observed in Figs. 2, 3 and 4.

IV-1. Ranges in which Size Increases with Temperature

Under vacuum as well as under water-vapor pressure, these ranges are located at higher temperatures. The curves in Fig. 5 show that at such temperatures an increase in the size of the crystallites obtained is observed related to the thermal treatment length. The most important increase occurs during the first 20 mins.

A phenomenon very similar to sintering brings about this increase of the sizes of the oxide crystallites once they are formed. Table II indeed shows the increase subsequent to formation. A treatment at 350°C for 18 hr of an oxide prepared at 150°C yields the same sizes as those of an oxide prepared directly at this temperature for the same time.

The temperature at which this kind of sintering occurs is lower if there is an increase of water-vapor pressure (Fig. 4). This effect on sintering of oxide powders by water vapor has already been shown by some authors (*7*).

Analyzing the experimental results we have up to now considered that the diffraction peak broadening is due only to a side effect of the oxide crystallites. This is generally admitted by authors using the diffraction peaks of such oxides. However, the fact that broadening might partially be due to some crystal defects (*16*) cannot be completely excluded. The diffraction peak profile narrowing observed in these temperature ranges might then be due to the removal of residual strains. Work is being done to clarify this point.

TABLE II

CRYSTALLITE SIZES D_{hkl} OF CdO OBTAINED, IN VACUUM, DIRECTLY AT THE PREPARATION TEMPERATURE Pr OR AFTER A TREATMENT AT A TEMPERATURE Tr ($t = 18$ HR FOR PREPARATION OR TREATMENT)

T (°C)	D_{111} (Å)	D_{200} (Å)	D_{220} (Å)
Pr:150	140	125	108
Pr:150 and Tr:150	140	124	108
Pr:150 and Tr:350	192	173	152
Pr:350	195	178	152

IV-2. Range in which Size Decreases with Temperature

This phenomenon is observed only when decomposition is carried out under a water-vapor atmosphere. In this temperature

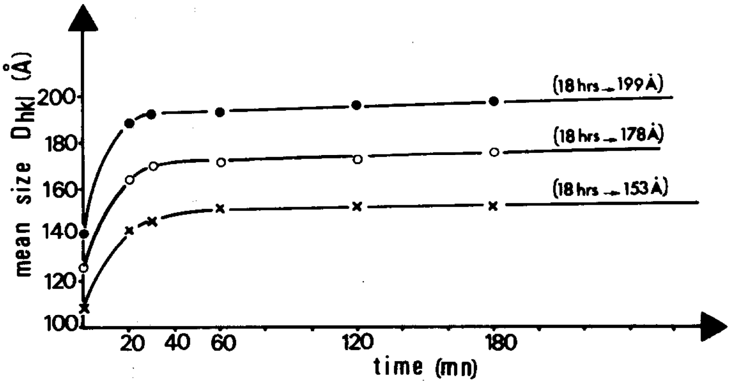

FIG. 5. Variation of mean crystallite sizes D_{hkl} vs decomposition time t, in vacuum, at $T = 355$°C: ● from 111 peak; ○ from 200 peak; × from 220 peak.

range, heating time has no influence on crystallite size. The sizes are exactly the same after 5 min or after 18 hr of thermal treatment. This observation, thus, does not seem to be due to the occurrence of a phenomenon following formation, but to be characteristic of the latter under water-vapor pressure. The experimental results listed in Table III, indeed, show that crystallites prepared under vacuum keep their dimensions when they undergo treatment at 180°C under $P = 5$ torr, i.e. in range *I*, where crystallite formation is, thus, solely responsible for the sizes observed; it is followed by no evolution.

The study of the structural transformation mode (see Section IV-3) has shown that it exhibits all the morphological and structural features of a transformation without diffusion. The experimental results discussed below seems to be opposed to such a reaction type. In this range, the higher the temperature, the smaller the crystallites, which means that the greater the decomposition rate, the smaller, the crystallites. These results would, on the contrary, validate the idea of a germination growth transformation, i.e. implying a diffusion of the chemical entities which will build up the new solid phase. Indeed when this transformation mode occurs the higher the rate the smaller the size of the crystallites produced.

Nevertheless in these experimental conditions the other structural characteristics of a transformation without diffusion are always observed. However it is possible to propose an interpretation for this observation consistent with a diffusionless transformation. In a transformation without diffusion such as the martensitic transformation, just before the formation of a crystallite of the produced solid, i.e. just before a fragmentation of the initial crystal, the strains brought about by the change of atomic configuration are exactly balanced by interatomic forces (*10*).

In the case of the present transformation, the crystallites of the solid produced are smaller than those produced by a classical martensitic transformation. For this reason a third kind of force must be taken into account, solid–gas superficial tension forces which are opposed to the fragmentation of the initial crystal. In vacuum these interactions between solid and atmosphere are certainly negligible. Thus the strengths are quite independent of temperature in the relatively narrow temperature range in which we are working. Thus the sizes of the crystallites produced under vacuum do not vary with temperature (next section). But under a water-vapor pressure the superficial interactions are more important and must decrease with temperature. Thus the sizes of

TABLE III

MEAN SIZES D_{hkl} OF CADMIUM OXIDE PREPARED AT T°C

	D_{hkl} (Å)								
	(a)			(b)			(c)		
T (°C)	*111*	*200*	*220*	*111*	*200*	*220*	*111*	*200*	*220*
180	139	125	108	215	189	166	140	123	108
255	138	125	107	199	176	148	168	149	131

(a) For 18 hr in vacuum.
(b) For 18 hr under $p_{H_2O} = 5$ torr.
(c) In vacuum and then treated for 18 hr under $p_{H_2O} = 5$ torr at the same temperature.
(180°C and 255°C are respectively in ranges I and II of Fig. 3).

the crystallites produced under a water-vapor pressure are larger than under vacuum and decrease with an increase of temperature.

IV-3. Ranges where Size is Independent of Temperature

In this range experiments lead us to make a distinction between what occurs under vacuum and water-vapor pressure. In the above section, it has been shown that the presence of water vapor brings about further phenomena when the oxide crystallites are formed. The following results will show that in the temperature range termed II even more complex phenomena influence the final dimensions of the oxide crystallites.

For understanding what happens, the influence of heating time has been studied. In Fig. 6 we can see that the crystallite size of the oxide produced in this temperature range increases with heating time but leads to a limit D_∞ and, surprising result, this limit D_∞ is independent of temperature. At the other end of the curve, extrapolation for time equal zero gives a limit D_0 which, on the contrary, is a function of temperature. This value D_0 is on the extension of the straight line which approximately describes D variations versus temperature in region I (Fig. 7). These results reveal, therefore, a particular evolution phenomenon; in this region II, as in region I, the initial oxide crystallite size, i.e. the size of oxide crystallites at their formation, decreases when decomposition temperature increases whereas in region II the final oxide crystallite size is independent of temperature.

Is this limited evolution of mean apparent crystallite size due to a resorption of residual strains or is it due to a decrease in surface defects? So far it is impossible to give a satisfactory explanation of this observation.

On the contrary, under vacuum, in the range 80–300°C, the results seem to be easier to explain. All over this temperature range crystallite sizes are independent of heating time (Table II at 150°C and Table IV); this means that, in these experimental conditions, the oxide crystallite formation occurs alone.

This analysis gives a great importance to the results listed in Fig. 2. The crystallites form with dimensions that are independent of temperature, thus independent of the reaction rate, which varies tremendously between 80°C and 300°C. A thorough study was made in those experimental conditions; it resulted in the following conclusion: the structural transformation associated with reaction $Cd(OH)_2 \rightarrow CdO$ does not involve any diffusion of the chemical entities which

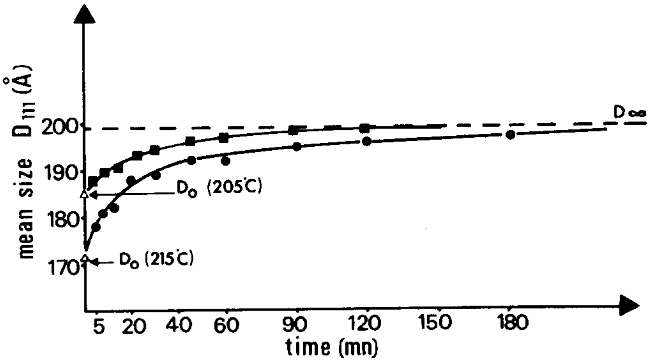

FIG. 6. Variation of mean crystallite size D_{111} vs decomposition time t in water vapor (P_{H_2O} = 5 torr) at two temperatures of region II (■ for 205°C; ● for 215°C). D_0 and D_∞ are the limits of D_{111} for $t = 0$ and $t = \infty$ respectively.

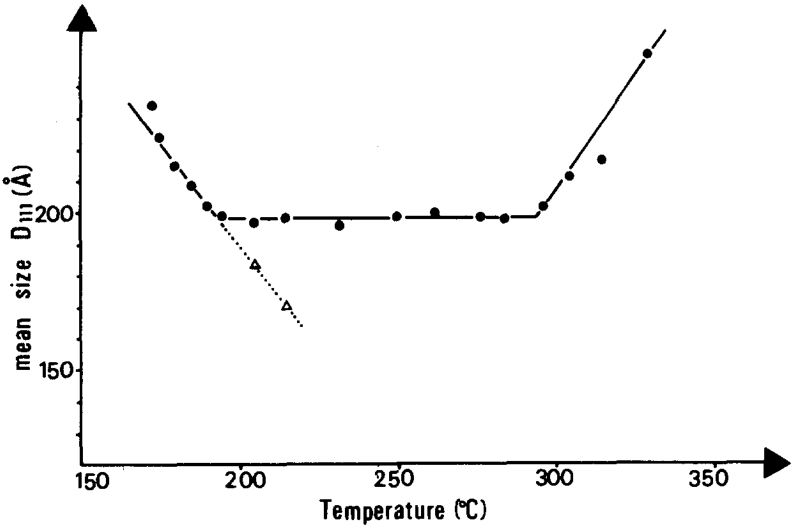

FIG. 7. Mean crystallite size D_{111} vs temperature ($P_{H_2O} = 5$ torr): ● decomposition time = 18 hr; △ decomposition time equal zero for $T = 205$°C and 215°C. Obtaining of D_0 is shown on Fig. 6.

will constitute the oxide (*17*) and shows the morphological and structural features specific to a shear transformation (*18*).

V. Conclusion

The study which has been already reported is useful to both fundamental and applied research.

Fundamentally it is not possible to determine a reaction mechanism when the latter is concealed by a subsequent process. Thus it is necessary to have a good knowledge of the conditions under which the mechanism sought is occurring alone. For example, Fig. 8 reveals that the structural transformation can only be studied in experimental conditions of domain IV.

For applied research the interest is also evident. For many utilizations of divided oxides it is necessary to check strictly some characteristics of these materials and particularly the sizes and the shape of the crystallites; the catalytic power of the suitability for sintering of a divided oxide are related in particular to the structural and morphological features of the crystallites. Thus it is necessary that the influence on the features of the oxide produced of experimental conditions in which decomposition is carried out are well known. For example in the studied case, the most divided oxide is obtained under vacuum.

Finally the example chosen for this study, the decomposition of cadmium hydroxide into oxide, is very suitable for obtaining a full diagram representing the influence of experimental conditions (Fig. 8). Indeed one can observe on this diagram that the starting decomposition curve (C) is located at

TABLE IV

MEAN CRYSTALLITE SIZES D_{hkl} VERSUS DECOMPOSITION TIME IN VACUUM AT $T = 150$°C

Time	D_{111} (Å)	D_{200} (Å)
25 mn	140	123
30 mn	138	125
45 mn	143	123
1 hr	142	125
1 hr 30	140	124
2 hr	138	125
3 hr	140	125
4 hr	138	123
5 hr	138	125
18 hr	140	125

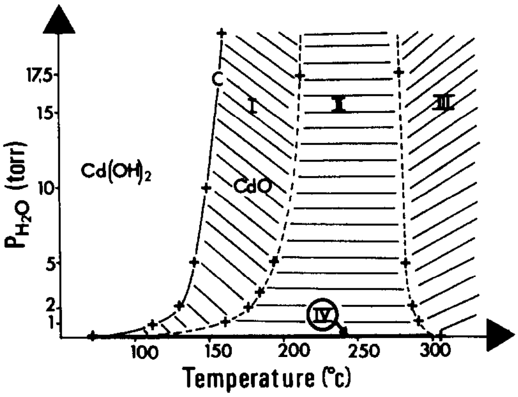

FIG. 8. Various areas in the P.T. diagram in which the formation of CdO crystallites from the $Cd(OH)_2$ precursor is associated or not with another phenomenon:

I. Formation is associated with an interaction solid water vapor but without any evolution with time

$D_{hkl} \searrow$ when $T \nearrow$ and $D_{hkl} \nearrow$ when $P \nearrow$.

II. Formation is associated with a particular evolution

$D_{hkl} = C^{st}$ when $T \nearrow$ and $D_{hkl} \nearrow$ when $P \nearrow$.

III. Formation is always associated with sintering.

IV. Formation happens alone

$D_{hkl} = C^{st}$ when $T \nearrow$.

C—Curve of starting decomposition, of $Cd(OH)_2$ into CdO. Hatching meaning: /////: crystallite size D_{hkl} increases with T; ≡: crystallite size D_{hkl} is constant with T; \\\\\\\\: crystallite size D_{hkl} decreases with T.

temperatures lower than those of the lower limit of region II. But if the starting decomposition curve had been located in domain II or even in domain III the observed evolution phenomena would escape investigation. We have studied various oxide-precursor pairs. For the MgO–$Mg(OH)_2$ pair this curve is very close to this region; the study of the mechanism is more difficult. But for many oxide–hydroxide or oxide–carbonate pairs this curve is situated at temperatures higher than those of the limit between II and III; in such cases the study of the mechanism is quite forbidding.

Acknowledgments

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