Thermochimica Acta, 142 (1989) 175–188
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

FORMATION OF AMORPHOUS $CaCO_3$ DURING THE REACTION OF CO_2 WITH CaO

MAREK MACIEJEWSKI

Warsaw University of Technology, Institute of Basic Chemistry, Noakowskiego 3, 00-662 Warsaw (Poland)

ARMIN RELLER

Institute for Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich (Switzerland)

(Received 20 June 1988)

ABSTRACT

The gas–solid reaction between CO_2 and activated CaO (obtained from the decomposition of calcite under vacuum conditions) leads to the formation of X-ray amorphous calcium carbonate. In the temperature range 560–590 K the exothermic recrystallization of the amorphous material is observed by DTA. Further related phenomena are characterized by X-ray diffraction and electron microscopy. The results reveal an easy and widely applicable preparative pathway for the formation of amorphous solids.

INTRODUCTION

As Thomas and Renshaw noted [1], the literature covering investigations on reactions of the type $A_s \rightarrow B_s + C_g$ and $A_s + B_g \rightarrow C_s$ contains some statements which, by their repeated citation, tend to become axiomatic. However, experimental evidence for these statements is often lacking. One of these statements deals with the possible existence of metastable phases during the course of heterogeneous solid state reactions. Whether or not such metastable phases adopt structures which are distinctly different from the structures of the final reaction products is a matter of importance, not only for the theoretical description of these processes, but also for technical reasons, i.e. for the controlled production of materials with small particle sizes and high activity as catalysts or adsorbents. There is no doubt that the experimental conditions under which decomposition processes are performed influence decisively the properties of the solid products, such as crystallite size and shape, surface area and pore distribution. Whether or not the newly formed product is metastable and transforms subsequently into a thermodynamically stable form has not been answered yet. If such metastable phases exist they must be characterized with respect to their crystallin-

0040-6031/89/$03.50

ity, morphology and thermodynamic stability (presence of strains). Owing to the fact that up to now only X-ray amorphous metastable phases have been described, these questions still remain unanswered.

Glasson [2,3] suggests the existence of three distinct steps during the decomposition of metal carbonates or metal hydroxides into metal oxides: (i) the formation of an oxide which exhibits a pseudolattice of the parent reactant; (ii) the recrystallization of this pseudolattice to the more stable normal lattice; (iii) the sintering of the recrystallized oxide. According to Glasson's opinion, the temperature and time of the dissociation as well as the actual ambient gas pressure influence the course of these particular reactions. In turn, the properties of the solid products formed depend directly on these parameters.

The idea of an 'active product' formed during the initial period of a decomposition is also discussed in detail by Gregg [4,5]. According to his statements, the 'activity', although difficult to define precisely, manifests itself through properties of the respective product, such as, for example, an enhanced reactivity towards gases or liquids, or an increased heat of dissolution in comparison with the values calculated from the normal heat of formation. Gregg suggests that two main factors are responsible for these features: (i) the presence of an extensive internal area of the solid established by the presence of micropores; (ii) the existence of lattice strains leading to small displacements of all atoms or ions from the positions they would occupy in the perfect, thermodynamically stable lattice of the solid product. These factors would also explain that at the beginning of a decomposition the product formed exhibits a pseudolattice, which recrystallizes during the course of decomposition.

The above-mentioned hypotheses have only been confirmed experimentally by the measurement of specific surface areas. Data have been determined by Mikhail et al. [6] on the decomposition of Iceland spar crystals ($CaCO_3$). They concluded that the initially formed CaO product phase exhibits a remarkably high surface area, which subsequently decreases sharply. However these results could not be confirmed by the experiments performed by Ewing et al. [7], who showed that the surface area of the CaO formed depends linearly on the progress of the decomposition reaction of the initial $CaCO_3$.

The presence of metastable solid products has also been introduced into kinetic considerations by Cremer and Nitsch [8] and Hyatt et al. [9]. Hyatt suggests that initially formed CaO adopts an unstable structural state between the parent rhombohedral $CaCO_3$ and the final, well-crystallized CaO. This assumption is based on kinetic data determined for the decomposition of $CaCO_3$ under CO_2 pressure. It has not been verified directly by complementary experiments.

The first experimental proof for the existence of such a metastable phase was presented by Rao and coworkers [10,11], who investigated the decomposition of a series of metal hydroxides and metal carbonates. They observed, by means of DTA measurements, an exothermic process directly after the endothermic decomposition. This exothermic process was attributed to the removal of internal structural defects in the metastable oxide lattice formed just after the decomposition of the parent materials. The estimated ΔH values of these relaxation and recrystallization processes were in the range 0.2–1.0 kcal mol^{-1}.

These results have not been confirmed in other published work. In hundreds of experiments Maciejewski [12] tried to find an analogous effect during the course of the thermal decomposition of $CaCO_3$. The experiments were performed over a wide temperature range (720–1250 K) and with varied pressure conditions. Although a highly sensitive apparatus was used, an exothermic effect following the decomposition process could not be found. Based on considerations included in ref. 13 it must be concluded that the fraction of the decomposed product surface covered with the metastable CaO phase is very small. The amount of this metastable phase becomes even smaller with increased partial pressures of CO_2. Moreover, the recrystallization of metastable CaO is very fast at the temperatures obtained during measurements under non-isothermal conditions. Thus the possibility of directly observing the exothermic recrystallization is minimal.

Apart from these findings and the above-mentioned experiments by Rao et al., further proof for the existence of metastable CaO formed during the degradation of $CaCO_3$ single crystals has been published by Beruto and Searcy [14,15]. They used the method of Langmuir for the determination of the vapour pressures of the evolved CO_2 and characterized the products obtained by scanning electron microscopy. They concluded that the initial phase formed during the process corresponds to a distinct layer of metastable CaO (thickness, 30 μm), which separates the undecomposed $CaCO_3$ from the well-crystallized product phase, i.e. the stable CaO. A few years after the publication of these results, they were withdrawn. The metastable phase obtained under vacuum conditions which exhibited similar unit cell dimensions to the parent $CaCO_3$, turned out to be poorly crystalline $Ca(OH)_2$, which was formed by the reaction of very active CaO with water vapour before the X-ray measurements could be completed. Further experiments [7] have proved that the very active CaO obtained during the decomposition of $CaCO_3$ under vacuum shows the well-known diffraction pattern. Owing to the extremely small particle sizes and as a result of the presence of only poor long-range order and of strains within the crystallites, the reflections of the X-ray patterns were very broad and their intensities were very low compared with those registered for CaO formed by the decomposition of $CaCO_3$ in air or CO_2.

These latter conclusions have been confirmed by Towe [16], who carried out in situ experiments in a transmission electron microscope. He observed the formation of very fine CaO needles with particle sizes around 100 Å and crystallographic parameters identical to those determined for CaO formed in air. In conclusion, the observed metastability and high reactivity of CaO is a consequence of the size and shape of the crystallites rather than a result of fundamental differences in its structural framework.

This short review of the literature data confirms that, as yet, no convincing experimental evidence exists for the formation of an amorphous and/or metastable phase during the course of the reversible reaction $CaCO_3 \rightleftarrows CaO + CO_2$. By assuming a high probability for a direct observation of such a phase during the back-reaction, i.e. the carbonation of activated CaO, we have set out to investigate this process by independent, complementary techniques. In the literature covering this reaction [17–21], the formation of metastable $CaCO_3$ during the carbonation of CaO with CO_2 has not been observed. However, the formation of amorphous calcium carbonate has been reported by rapid precipitation techniques from highly supersaturated solutions containing Ca^{2+} and CO_3^{2-} ions [22].

RESULTS AND DISCUSSION

The course of the thermal decomposition of $CaCO_3$ under isothermal conditions and a reduced pressure of 10^{-4} kPa is presented in Fig. 1. The carbonation of the highly active CaO formed starts at 315 K under the selected experimental conditions (Fig. 2). Close to 570 K, a rapid increase in reaction rate is observed by a distinct peak of the DTG curve. As DTA

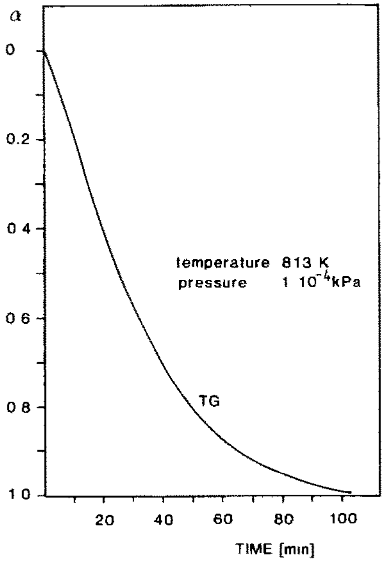

Fig. 1. Thermogravimetric measurement of the isothermal decomposition $CaCO_3 \rightarrow CaO + CO_2$ under vacuum conditions ($p = 10^{-4}$ kPa).

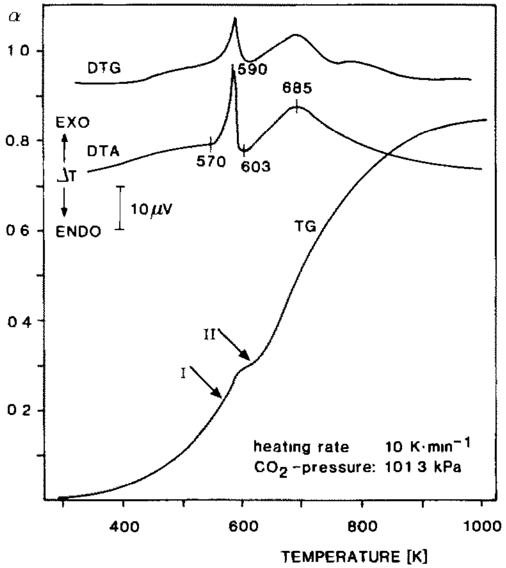

Fig. 2. Thermogravimetric measurement of the carbonation process $CaO + CO_2 \rightarrow CaCO_3$ under atmospheric pressure of CO_2. The parent CaO was obtained by decomposition of $CaCO_3$ under vacuum conditions (see Fig. 1). I and II indicate the positions where material was isolated for further investigation.

reveals, this process is exothermic. The carbonation is characterized by a short decrease in reaction rate in the temperature range 590–603 K. Subsequently, the rate increases again reaching a maximum at 685 K. Above this temperature, the reaction rate finally slows down to zero. In order to check whether the conditions of the $CaCO_3$ decomposition, and thus the type of CaCO formed, influences the course of the carbonation process, analogous measurements were performed using CaO obtained under different pressure conditions. The results of these investigations are summarized in Fig. 3. The carbonation of the CaO formed depends on the partial pressure of the inert gas during the decomposition of $CaCO_3$. The area of the exothermic peak observed around 580 K gradually decreases for the carbonation of CaO obtained under increasing pressures of inert gas (curve a, carbonation of CaO obtained under 10^{-4} kPa of N_2; curve b, carbonation of CaO obtained under 0.1 kPa of N_2; curve c, carbonation of CaO obtained under 101.3 kPa of N_2).

The ratio between the area of the exothermic DTA peak and the increase in mass observed by the TG signal proves that the amount of heat evolved in the temperature range 543–593 K is larger than that which would refer to the mere increase in the reaction rate of the CaO carbonation. An explanation for this phenomenon must be based on the assumption that in this temperature range the recrystallization of amorphous $CaCO_3$ leads to the registered exothermic DTA signal. In order to verify this hypothesis, X-ray diffraction measurements were carried out on $CaCO_3$ samples obtained

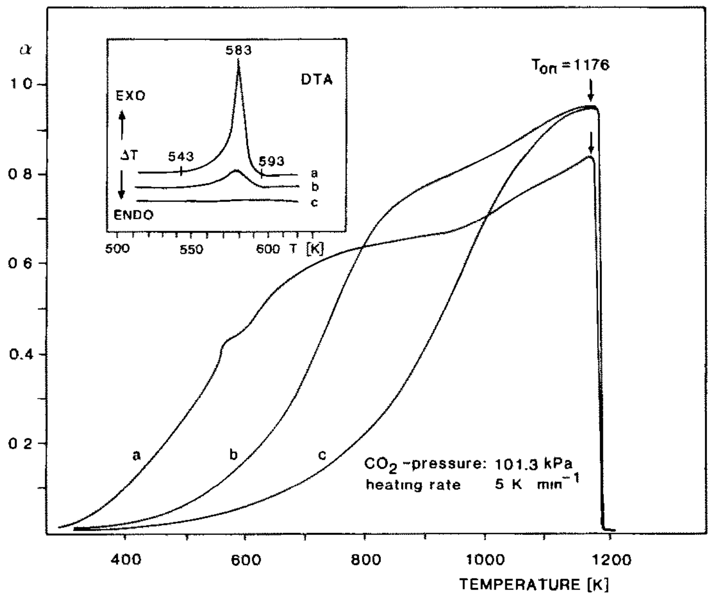

Fig. 3. TG and DTA measurements of the carbonation reaction $CaO + CO_2 \rightarrow CaCO_3$ as a function of the properties of the parent CaO, and the subsequent decomposition of the product $CaCO_3$ at elevated temperatures. For measurement a, parent CaO was obtained by isothermal decomposition of $CaCO_3$ under vacuum conditions ($T = 803$ K, $p = 10^{-4}$ kPa); for curve b, parent CaO was obtained by isothermal decomposition of $CaCO_3$ under partial pressure of N_2 ($T = 883$ K, $p = 0.1$ kPa); for measurement c, parent CaO was obtained by isothermal decomposition of $CaCO_3$ at 963 K under atmospheric pressure of N_2.

under identical experimental conditions by the reaction of highly active CaO with CO_2. In the first experiment, the carbonation was interrupted before the occurrence of the exothermic process (see Fig. 2, position I) and in the second experiment, the carbonation was interrupted directly after the occurrence of the exothermic process (see Fig. 2, position II). In the sample obtained at position I, only the parent product CaO can be identified as a crystalline phase. In the sample obtained at position II, i.e. after the exothermic process, calcite and CaO can be identified unambiguously. Owing to the fact that the amount of $CaCO_3$ formed during the second experiment ($\alpha = 0.30$) exceeds that formed during the first experiment ($\alpha = 0.23$), it could be argued that the presence of the crystalline $CaCO_3$ in the second sample is a mere consequence of the larger amount formed. To determine whether or not this is true the following measurement was performed. After producing around 25% $CaCO_3$ under the above-mentioned experimental conditions (i.e. by taking highly active CaO as the parent product and by interrupting the carbonation at 555 K) the reaction chamber was evacuated and cooled to room temperature. Subsequently, the chamber was refilled with pure nitrogen up to a pressure of 101.3 kPa and the temperature was raised at a heating rate of 10 K min^{-1}. The TG measure-

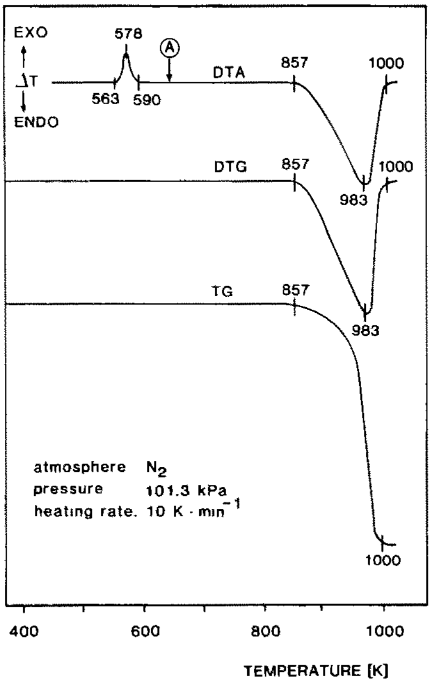

Fig. 4. TG and DTA measurements revealing the thermal behaviour of CaO and $CaCO_3$ isolated at position I (see Fig. 2) in pure N_2. Point A indicates the temperature at which the sample was isolated for X-ray diffraction studies.

ment shows no weight loss right to the onset temperature for the decomposition of calcite under the given conditions at around 860 K (Fig. 4). However, in the temperature range 563–590 K a sharp exothermic DTA peak is registered. This signal corresponds to the exothermic recrystallization of the amorphous $CaCO_3$. The X-ray analysis of a sample isolated at point A in Fig. 4, i.e. after the exothermic recrystallization, clearly reveals the presence of crystalline calcite.

During the experiments performed under non-isothermal conditions, the maximum amount of $CaCO_3$ formed before the occurrence of the exo-effect depends on the heating rate and lies in the range 22%–35% of the total conversion. In order to increase the amount of amorphous $CaCO_3$, experiments under isothermal conditions were carried out. The carbonation of highly active CaO was investigated at 473 K. At this temperature, about 50% of the parent CaO reacts with CO_2 after 12 h. In Fig. 5, the X-ray diffraction patterns of samples isolated before the occurrence of the exothermic recrystallization (pattern a) and after recrystallization under N_2 (pattern b) are summarized. Even for samples containing 64% $CaCO_3$, no crystalline portions are observed before the exothermic recrystallization. After this exothermic process, the calcite lines can always be clearly identified.

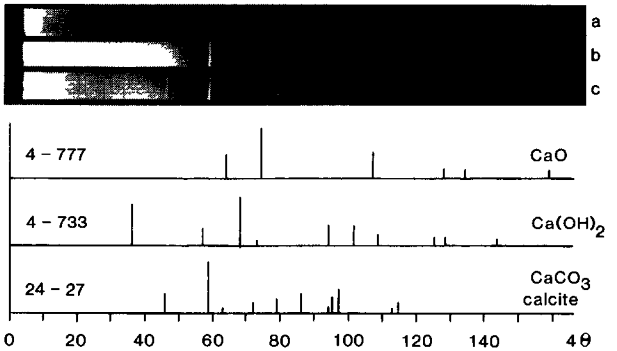

Fig. 5. X-ray diffraction patterns of a sample produced by 50% carbonation of highly active CaO at 473 K (pattern a, only reflections of CaO can be identified); the same sample after heat treatment in N_2 at 600 K, i.e. after recrystallization (pattern b, reflections of CaO and calcite ($CaCO_3$) are present). In pattern c, the reflections of standard material ($CaCO_3$, Merck, pro Analysi) are presented. As a reference the diffraction patterns of CaO, $Ca(OH)_2$ and $CaCO_3$ (calcite) are displayed schematically.

The heat of crystallization of amorphous $CaCO_3$ was measured using DSC. A typical measurement is presented in Fig. 6. The value for ΔH lies in the region of 2 kcal/mol^{-1}. The DSC measurement presented in this paper represents only the order of magnitude of such processes. More accurate data will be published later [23]. It must be noted that accurate measurements of ΔH values are difficult, since uncontrolled reactions of the highly active CaO remaining with water vapour or with atmospheric CO_2 have to be ruled out during all transfer and measuring procedures.

As scanning electron microscopic studies reveal, the morphology of CaO formed by the decomposition of calcite under vacuum conditions (Fig. 7) is

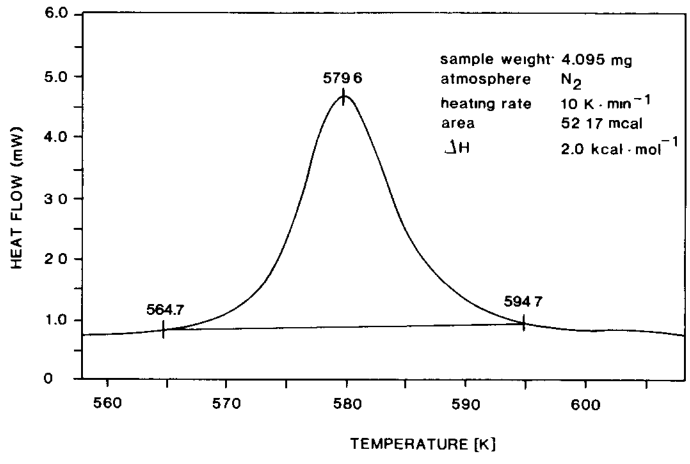

Fig. 6. DSC measurement representing the exothermic recrystallization of amorphous, metastable $CaCO_3$ into well-crystallized calcite.

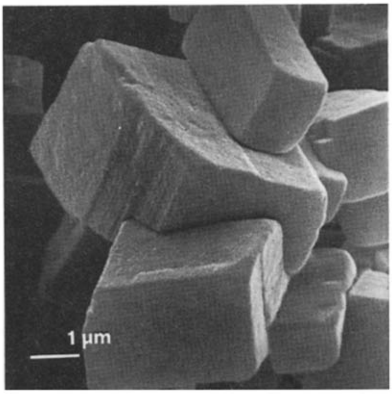

Fig. 7. Scanning electron micrograph revealing the morphology of CaO, which was produced by the thermal decomposition of calcite under vacuum conditions (see Fig. 8).

very similar to that of parent calcite crystallites (Fig. 8). This fact allows a semiquantitative determination of the thickness of the layer of amorphous $CaCO_3$ formed during the carbonation process. Taking a crystallite of CaO with edge dimensions of 10 μm, the volume of the amorphous $CaCO_3$ formed at $\alpha = 0.33$ equals one-third of the total volume. At this point, the edge dimensions of the as yet unreacted CaO decrease from 10 μm to 8.73 μm. Accordingly, the thickness of the amorphous $CaCO_3$ layer lies in the region of 0.65 μm.

Morphological studies by transmission electron microscopy using replica techniques are summarized in Figs. 9(a)–9(d). Micrograph 9(a) shows the surface of a part of a CaO crystallite covered by an amorphous $CaCO_3$ layer, i.e. before recrystallization has occurred. The micrographs 9(b)–9(d) reveal the morphology of an analogous region after recrystallization under nitrogen has occurred. For both samples, the degree of carbonation was 30%. The micrographs of the recrystallized surfaces somehow indicate the

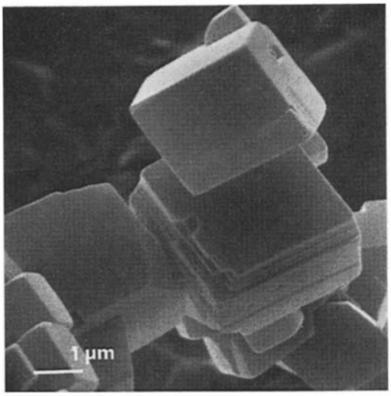

Fig. 8. Scanning electron micrograph of calcite crystallites used for the experiments.

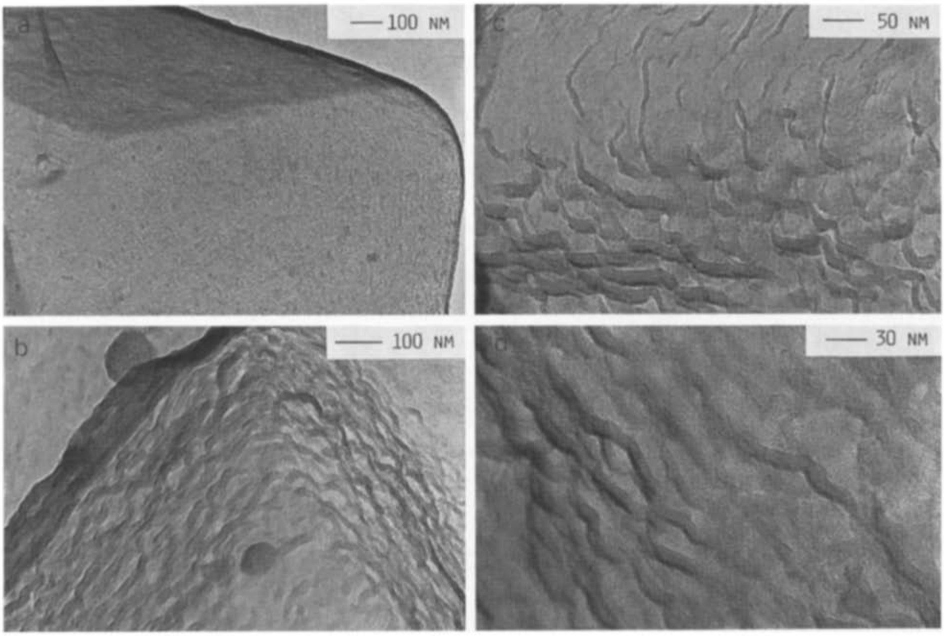

Fig. 9. Transmission electron micrographs (replica technique) of: (a) a CaO–$CaCO_3$ sample covered with amorphous $CaCO_3$ (conversion, 30%); (b)–(d) a similar sample after the recrystallization of the amorphous layer under nitrogen ((b)–(d), increasing magnification).

characteristic features of the morphology of calcite crystallites, i.e. their rhombohedral shape. The measured increase in carbonation rate during the exothermic recrystallization (Fig. 2, TG and DTG signals in the temperature range 560–590 K) can therefore be explained by a less hindered diffusion of CO_2 to the unreacted CaO through the less compact product layer.

High resolution electron microscopy provides evidence that the domains of the recrystallized calcite are very small, i.e. with diameters in the range 5–10 nm (Fig. 10). These dimensions strongly depend on the experimental conditions under which the sample is obtained. However, within the domains the well-known calcite structure is adopted as revealed by selected area electron diffraction and X-ray diffraction.

In earlier experiments performed by Maciejewski and Oswald [24] it has been shown that calcium oxide obtained from the decomposition of $CaCO_3$ exhibits two kinds of pores. The formation of these pores depends directly on the experimental conditions during the decomposition process. This phenomenon has also been described by Beruto and coworkers [25,26]. In the highly active CaO, pores with cross-sections in the region of $< 10^{-2}$ μm are present [7]. They can hardly be distinguished by scanning electron microscopy (see, e.g., Fig. 7 in this paper or Fig. 3 of ref. 15). However, in CaO obtained from the decomposition of $CaCO_3$ under an inert gas atmosphere or under CO_2 pressures, pores with cross-sections in the range 0.1–0.3 μm are found (see Figs. 11 and 12).

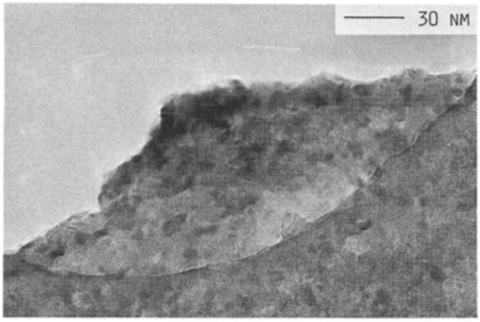

Fig. 10. High resolution electron micrograph of a section of recrystallized $CaCO_3$ revealing single-crystalline domains with dimensions of <10 nm.

These morphological features account for the influence of the different experimental conditions on product formation. Moreover, they explain the distinct carbonation behaviour of the parent CaO products. For highly active CaO formed under vacuum conditions, the reaction with CO_2 (under non-isothermal conditions) starts at very low temperatures, i.e. below 320 K, and increases steadily until the recrystallization of the product layer. After the recrystallization, the reaction rate decreases; the reversible process is diffusion and temperature controlled. For CaO obtained under higher pressure, the carbonation is much slower at low temperatures, i.e. the CaO formed is much less reactive towards CO_2. However, owing to the presence of large pores the carbonation proceeds comparatively quickly at elevated temperatures. The diffusion of CO_2 to the unreacted CaO is less hindered.

The results presented above provide evidence that the existence of meta-stable and/or amorphous phases during the course of heterogeneous solid state reactions can be observed by experiments carried out under non-isothermal and, in certain cases, under isothermal conditions. Moreover, the

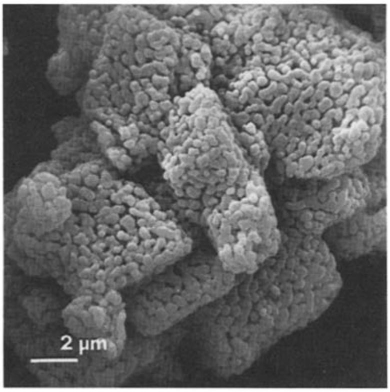

Fig. 11. Scanning electron micrograph of pseudomorphous CaO obtained by isothermal decomposition of calcite crystallites under N_2 ($T = 900$ K; $p = 101.3$ kPa).

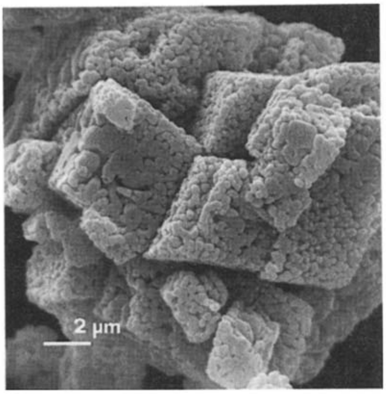

Fig. 12. Scanning electron micrograph of pseudomorphous CaO obtained by isothermal decomposition of calcite crystallites under CO_2 ($T = 1023$ K; $p = 1$ kPa).

results also explain why the metastable and/or amorphous phases have not yet been described in the related literature. During the course of reactions performed at comparatively high temperatures, e.g. for the carbonation of CaO usually in the range 800–1000 K, it is not possible to isolate the amorphous, metastable phase, because all the $CaCO_3$ produced is immediately converted into the well-crystallized form. In turn, parent CaO, which has been formed by the decomposition of $CaCO_3$ under normal pressure conditions, i.e. not under vacuum, exhibits a much lower activity towards carbonation in CO_2. Accordingly, at a low temperature of around 570 K, the amount of amorphous $CaCO_3$ formed during the carbonation of such relatively inactive CaO is very small. As shown experimentally (Fig. 3, curve c), this metastable $CaCO_3$ is not even detectable.

In summary, our experimental findings reveal that an excess of energy is stored within amorphous phases. This energy renders the material metastable and it is released during the recrystallization process. The two principles for the production of such metastable phases via heterogeneous solid state reactions can be summarized as follows: (i) the production of a highly active parent reactant by the decomposition of an appropriate precursor material under vacuum conditions and (ii) the performance of the solid–gas (back-)reaction at temperatures as low as possible, e.g. for the reaction $CaO + CO_2 \rightarrow CaCO_3$ below 500 K.

The temperatures of recrystallization vary from one compound to another. Our experiments on analogous processes in the strontium and barium systems yield recrystallization temperatures in the range 520–600 K [23]. Quantitative measurements on the reactivity of the highly active CaO, i.e. conversions with low partial pressures of CO_2 and with CO_2–H_2O mixtures, will be published later [23].

CONCLUSIONS

Depending on the experimental conditions during the thermal decomposition of $CaCO_3$, the solid CaO phase produced adopts different properties. Among these properties, its reactivity towards CO_2 is most remarkable. CaO obtained under vacuum conditions is highly active and undergoes carbonation with CO_2 even at temperatures as low as 320 K. The product $CaCO_3$ phase obtained by this low temperature reaction proves to be X-ray amorphous. For samples containing 50% of $CaCO_3$, only reflections of the parent CaO can be identified by X-ray diffractometry. In the temperature range 560–590 K this amorphous and metastable $CaCO_3$ transforms via an exothermic process into well-crystallized calcite. During the recrystallization, the diffusion rate of CO_2 through the newly formed product layer is enhanced.

The morphology of the parent CaO greatly influences the course of the carbonation process. The presence of large pores within the parent reactant leads to comparatively high carbonation rates at high temperatures. Such large pores are obtained if CaO is formed under ambient pressure conditions in CO_2 or N_2 atmospheres. The $CaCO_3$ produced by the carbonation of CaO formed under these conditions proves to be crystalline (comparatively high temperature of formation and low rate of formation at low temperatures).

Under non-isothermal conditions amorphous, metastable $CaCO_3$ can only be produced in larger amounts if highly active CaO is used as material for the carbonation. This fact, as well as the comparatively low temperature of recrystallization, represent the main reasons for the absence of experimental confirmation for the existence of amorphous, metastable $CaCO_3$ in the literature. The results described may open up new possibilities for the identification and, therefore, the possible isolation of further amorphous compounds during reversible heterogeneous solid state reactions.

EXPERIMENTAL

The course of the reactions were investigated using a Mettler 2000C thermoanalyser. Samples of polycrystalline $CaCO_3$ (Merck p.A.) were fully decomposed to CaO under dynamic vacuum conditions ($p = 10^{-4}$ kPa) in the temperature range 803–843 K. After cooling the solid product under vacuum to room temperature, the system was refilled with CO_2 to a pressure of 101.3 kPa. The carbonation of the CaO thus formed was performed with heating rates of 5K min^{-1} and 10 K min^{-1} respectively.

X-ray diffractometry was carried out on a Guinier IV camera FR 552 equipped with a Johansson monochromator (Nonius, Delft) using Cu $K\alpha_1$ radiation. The intensities of the reflections were measured on a double-beam recording densitometer MK IIICS (Joyce, England).

Scanning electron micrographs were taken on a Stereoscan SI (Cambridge Instruments, England). Transmission electron micrographs were taken using a Hitachi HU 125 microscope and high resolution electron microscopy was carried out using a JEOL 200CX microscope.

Differential thermal analysis was carried out using a Mettler 2000B thermoanalyser, and differential scanning calorimetry was performed on a 7 Series Thermal Analysis System (Perkin–Elmer, U.S.A.).

ACKNOWLEDGEMENTS

Financial support for one of the authors (M.M.) from the 'Bundesamt für Energiewirtschaft' is highly appreciated. The authors express their gratitude to A. Portmann for his substantial contributions to the electron microscopic studies.

REFERENCES

1 J.M. Thomas and G. Renshaw, J. Chem. Soc., Chem. Commun., (1967) 2058.
2 D. Glasson, J. Chem. Soc., Chem. Commun., (1956) 1506.
3 D. Glasson, J. Appl. Chem., 8 (1958) 793.
4 S. Gregg, J. Chem. Soc., Chem. Commun., (1953) 3940, 3945.
5 S. Gregg, J. Chem. Soc., Chem. Commun., (1955) 46, 3804.
6 R. Mikhail, S. Hanafi, S. Abo-El-Enein, R. Good and J. Irani, J. Colloid Interface Sci., 75 (1980) 74.
7 J. Ewing, D. Beruto and A. Searcy, J. Am. Ceram. Soc., 62 (1979) 580.
8 E. Cremer and W. Nitsch, Z. Elektrochem., 66 (1962) 697.
9 E. Hyatt, I. Cutler and M. Wadsworth, J. Am. Ceram. Soc., 41 (1958) 70.
10 C.N.R. Rao and K. Pitzer, J. Phys. Chem., 64 (1960) 282.
11 C.N.R. Rao, S. Yoganarashiman and M. Lewis, Can. J. Chem., 38 (1960) 2359.
12 M. Maciejewski, Thermal Decomposition of Solids—Determination, Reliability and Usefulness of Kinetic Parameters, Wyd. Politechniki Warozawskiej, Chemia Z. 44, Warsaw, 1988 (in Polish).
13 M. Maciejewski and J. Baldyga, Thermochim. Acta, 97 (1985) 105.
14 D. Beruto and A. Searcy, J. Chem. Soc., Faraday Trans. 1, 70 (1974) 2145.
15 D. Beruto and A. Searcy, Nature (London), 263 (1976) 221.
16 K. Towe, Nature (London), 274 (1978) 239.
17 J. Wuhrer and T. Langauer, Tonind. Ztg., 81 (1957) 332.
18 E. Cremer and W. Nitsch, Tonind. Ztg., 83 (1959) 579.
19 R. Barker, J. Appl. Chem. Biotechnol., 23 (1973) 733.
20 W. Oakeson and I. Cutler, J. Am. Ceram. Soc., 62 (1979) 556.
21 D. Beruto, M. Kim and L. Barco, J. Am. Ceram. Soc., 67 (1984) 274.
22 T. Ogino, T. Suzuki and K. Sawada, Geochim. Cosmochim. Acta, 51 (1987) 2757.
23 M. Maciejewski and A. Reller, Thermochim. Acta, in press.
24 M. Maciejewski and H.R. Oswald, Thermochim. Acta, 85 (1985) 39.
25 D. Beruto, L. Barco, A. Searcy and G. Spinolo, J. Am. Ceram. Soc., 63 (1980) 439.
26 D. Beruto, L. Barco and A. Searcy, J. Am. Ceram. Soc., 66 (1983) 893.