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Decarbonation and recarbonation of calcites heated in CO_2. Part 1. Effect of the thermal regime

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Abstract

Scanning electron micrographs and thermal analysis curves were obtained from a sample of synthetic calcite that was exposed to a series of heating and cooling cycles in CO_2 at just above atmospheric pressure. The heating rate, the maximum temperature of heating and the residence time at maximum temperature were varied. Scanning electron micrographs revealed that the morphology of the sample changed drastically even after a single heating cycle, but subsequent changes were much smaller, whatever the heat treatment. In contrast, very different thermal analysis curves were obtained. In the first heating cycle calcite decomposed within a narrow temperature range, giving a single, sharp endotherm. An exothermic signal on cooling was due to recarbonation, which occurred abruptly, probably on the surfaces of the particles. An additional small exotherm on the cooling curve was attributed to recrystallisation of poorly crystallised calcium carbonate. In subsequent heating cycles recarbonation partly overlapped decomposition of calcite. Some CO_2 was trapped in pores and more calcite formed as the temperature and pressure in the pores were raised. Depending on the heating regime, one, two or three endotherms resulted.

INTRODUCTION

The decomposition of calcite is probably the most intensively studied reaction of the type $X_{solid} \rightarrow Y_{solid} + Z_{gas}$. By 1987 no less than 168 different values of the activation energy for the decomposition reaction were reported in the literature [1]. Many more publications dealt with other aspects of the reaction and the properties of the CaO formed. The recarbonation reaction has received far less attention, no doubt due to its smaller practical importance. More research was devoted to sulphonation reactions of the calcined material, because of the application of this process for removal of sulphur-containing gases for environmental protection.

Despite the abundance of data, or perhaps because of it, some uncertainty concerning the mechanism of the calcination and the properties of the

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product still persists. It is generally agreed that the nature of the starting material and the conditions of the experiment, in particular the partial pressure of CO_2, affect the reaction kinetics and the properties of the CaO formed. The specific volume of CaO is less than that of calcite and the CaO formed by decalcination is porous. The porosity and the amount of sintering of the decomposing calcite and of the CaO produced depend on the thermal regime, on the partial pressure of CO_2 [2,3] and on the degree of contact between the particles [4]. The importance of the heating rate as an experimental variable has been pointed out, for example, by Borgwardt and co-workers, who showed that the surface area of CaO produced by rapid calcination is larger by an order of magnitude than that obtained on slow heating [4–6]. Nevertheless this parameter frequently appears to have been disregarded. Thus Maciejewski and Reller [7] noted an unexplained discrepancy in the values of surface areas of CaO determined by Mikhail et al. [8] and by Ewing et al. [2]. In neither of these papers are heating rates specified, though differences between them could easily account for the observed discrepancies.

The question arises whether the properties of the recarbonated phase are affected by the experimental conditions of the decarbonation and recarbonation reactions. This is both of intrinsic interest and can throw light on the reactivity of the calcined phase with CO_2 and other gases.

The present paper reports the results of an exploratory study of this problem, based on thermal analysis and scanning electron microscopy. Repeated heating and cooling cycles were carried out under a CO_2 atmosphere with the following variables: (1) the heating rate, (2) the maximum temperature of heating and (3) the time at maximum temperature.

EXPERIMENTAL

The starting material

The calcite used was A.R. grade precipitated $CaCO_3$ supplied by Riedel de Haen A.G. An Inductively Coupled Plasma (ICP) analysis confirmed that the purity did, indeed, conform to the manufacturer's specifications. Scanning electron micrographs showed that the sample contained some well-formed rhombs, but rhombohedral particles with perforated, indented and undulated surfaces and rounded edges were common (Figs. 1(a) and (b)).

The thermal regime

Samples were heated and cooled in a Stanton–Redcroft DTA/TG/DTG thermoanalyser (STA 780) under a stream of dried CO_2 at just above atmospheric pressure. About 20 mg of starting material were gently tapped

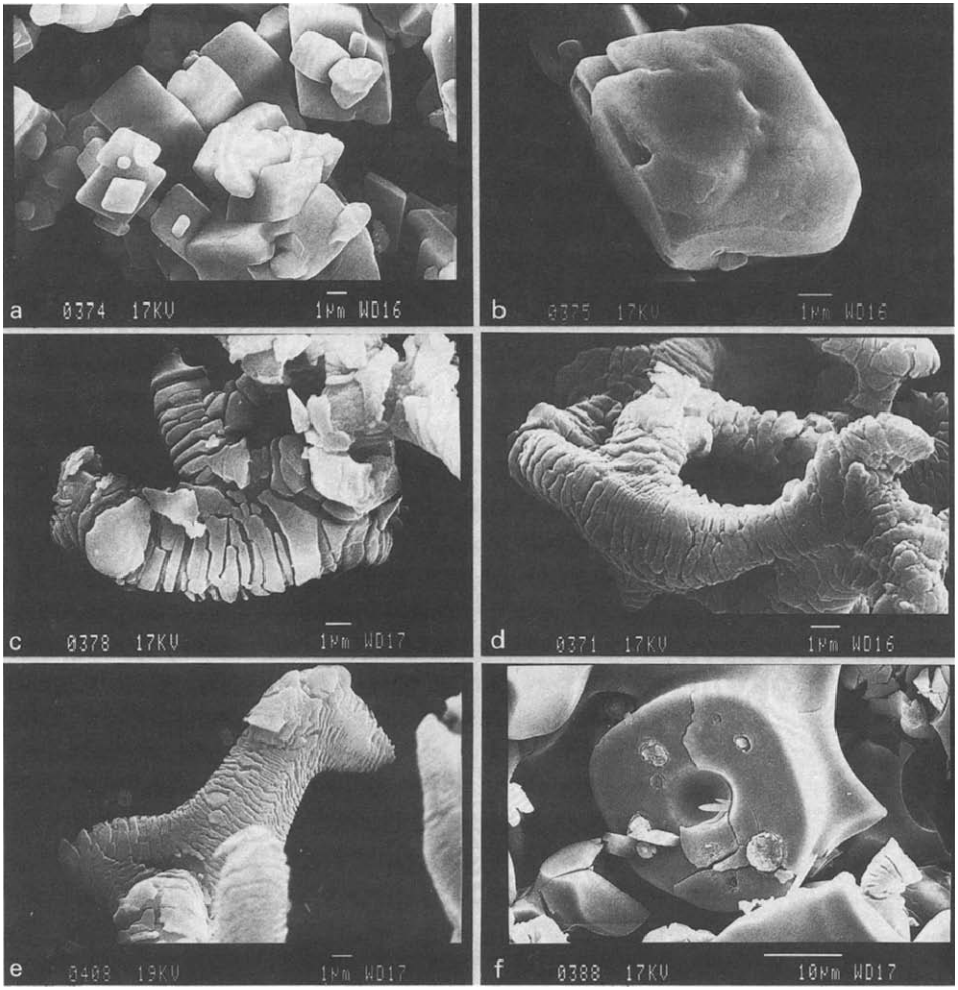

Fig. 1. Scanning electron micrographs of calcite; (a) and (b) original sample; (c) heated to 1170 °C and cooled; (d) heated 240 min at 1170 °C and subsequently taken through 30 cooling–heating cycles; (e) heated 5 min at 1170 °C and subsequently taken through 11 cooling–heating cycles; (f) heated to 1170 °C, cooled and reheated to 880 °C, where it was maintained for 18 h. Heating rate was 30 °C min^{-1}.

into a platinum crucible. The heating regime covered several variables which affected the decomposing calcite, the CaO formed or both.

(1) The heating and cooling rates ranged from 2.5 to 50 °C min^{-1}. Different heating and cooling rates are expected to affect the kinetics of the decarbonation and recarbonation reactions and the nature of the solids formed.

(2) The maximum furnace temperature attained in the heating cycles was either 1170 or 1270 °C. Decomposition of the calcium carbonate was complete below 1170 °C and heating to the higher temperature could only affect the nature of the CaO formed. Experiments in which the sample was

maintained at 1170 °C for various periods of time, up to 240 min, and subsequently cycled at the rate of 30 °C min^{-1}, were designed to test the effect of static heating on the reactivity of the CaO formed.

RESULTS AND INTERPRETATION

Selected heating cycles of three representative DTA/TG curves are shown in Figs. 2–4. Figure 2 was obtained by cycling at 30 °C min^{-1} from 550 to 1170 °C. Faster heating rates, up to 50 °C min^{-1}, gave rise to very similar curves. Figure 3 was recorded on cycling through the same temperature range at a much slower heating rate (5 °C min^{-1}). Similar curves were obtained when the heating rate was reduced to 2.5 °C min^{-1}. Figure 4 shows the curves produced by cycling from 550 to 1270 °C at a heating rate of 30 °C min^{-1}. Figures 5–7 present some of the data derived from these curves.

Table 1 summarises some of the results obtained when samples were maintained at 1170 °C for various periods of time before cooling and heating cycles commenced.

The significance of the various peaks is discussed below, but even a cursory examination of the figures and table shows that all the variables, i.e. the heating rate, the maximum temperature of the heating–cooling cycles, the number of cycles and the residence time of the CaO at maximum temperature, affect the course of the decarbonation and recarbonation

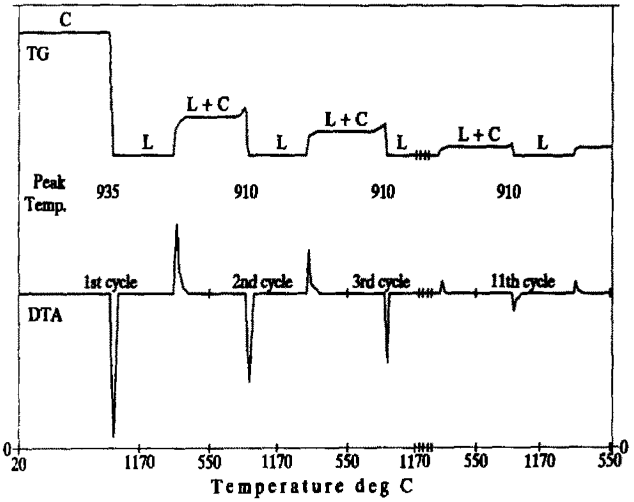

Fig. 2. TG and DTA curves of sample cycled between 550 and 1170 °C at 30 °C min^{-1}. The first three and the eleventh cycle are shown. Abbreviations: C, calcite; L, lime; Peak Temp., temperature of endotherm.

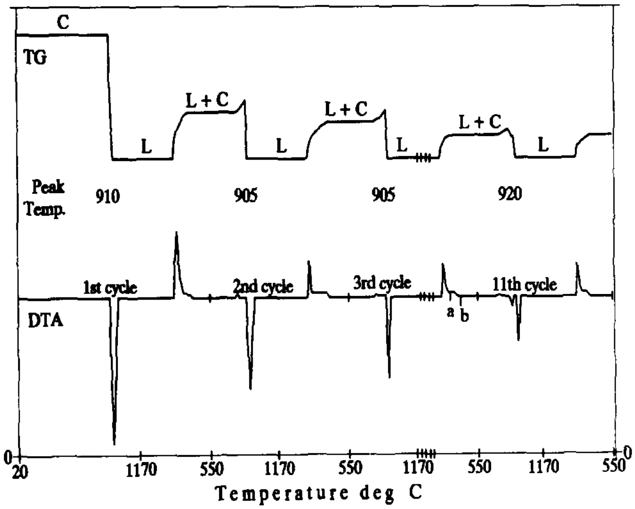

Fig. 3. Legend as for Fig. 2, but heating rate was 5 °C min^{-1}. Peak Temp., temperature of first endotherm.

processes. The exothermic and endothermic peaks reflect shifts in the reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (1)$$

to the left or right respectively.

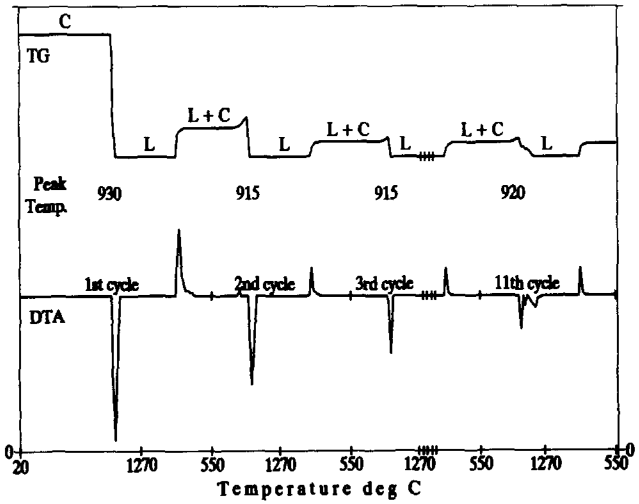

Fig. 4. Legend as for Fig. 2, but temperature range is 550–1270 °C. Peak Temp., temperature of first endotherm.

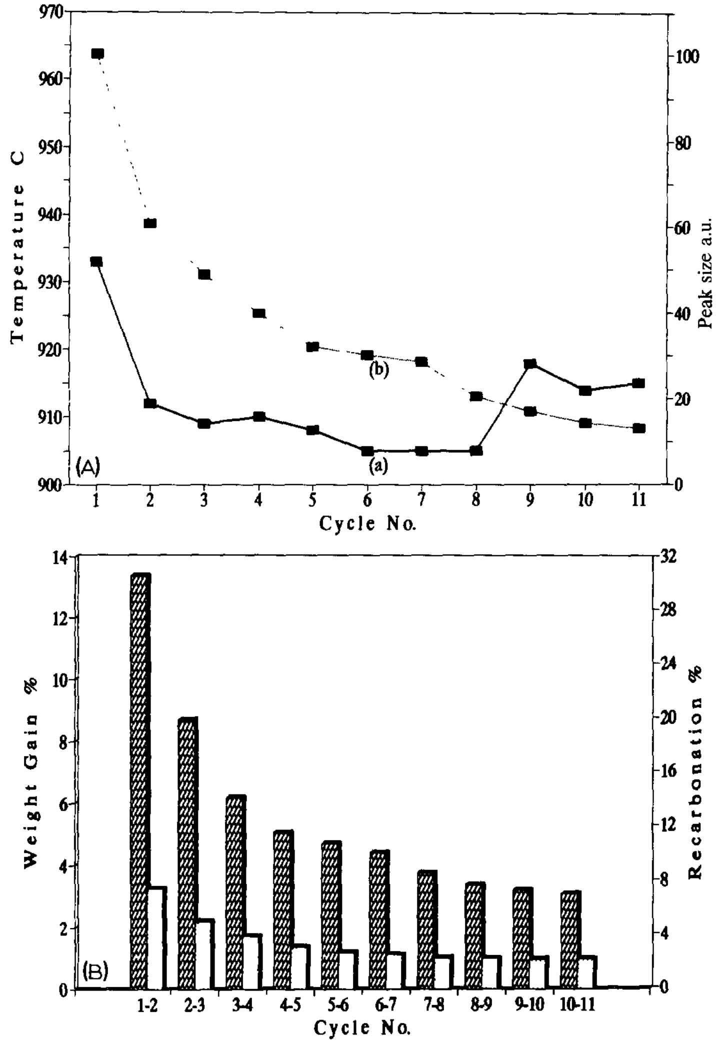

Fig. 5. Data derived from DTA/TG curves. Temperature range, 550–1170 °C; heating rate, 30 °C min^{-1} (cf. Fig. 2). (A) Peak temperature (a) and peak size (b) of endotherm. (B) Weight gain on cooling (cobblestone pattern) and on heating (stippled pattern).

Decarbonation, first cycle

In the first heating cycle all the samples gave rise to a large, sharp endotherm. The peak temperature ranged from 900 to 940 °C, depending on the heating rate. Heating in CO_2 rather than in an inert atmosphere not only raised the decomposition temperature, as expected, but also sharpened the departure from the baseline. This feature was noted previously, but no explanation was offered [9]. The endotherm was associated with a weight loss of 44%, corresponding to complete decarbonation. It is well established

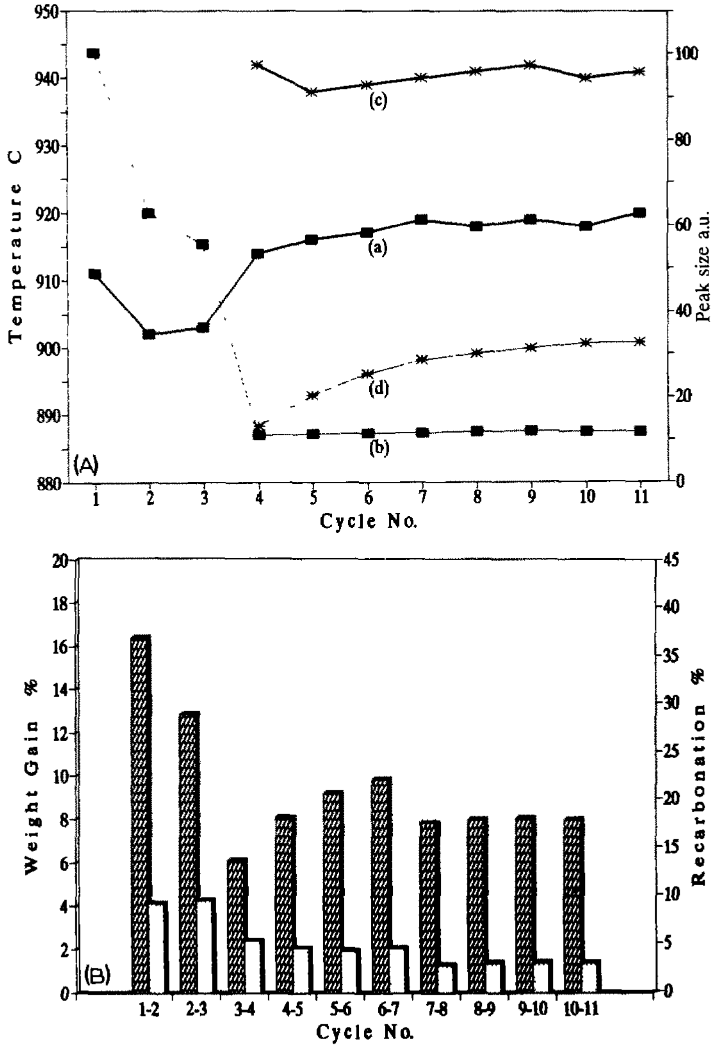

Fig. 6. Legend as for Fig. 5, but heating rate was 5 °C min^{-1} (cf. Fig. 3): ■, first ((a) and (b)); *, second ((c) and (d)) endotherms.

that the calcite undergoes a phase transition at elevated temperature [10]. This phase transition has only been documented for pressures above atmospheric; the extrapolated transition temperature at atmospheric pressure was 987 °C [11]. It seems possible that the sharpness of the endotherm may be due to a phase transition immediately followed by complete decomposition of the calcite, although the peak temperature appears to be too low.

In some runs a minute endotherm preceded the main peak. This could, perhaps, be attributed to decomposition of some very finely divided material, but a range of particle sizes would then be expected, with a concomitant

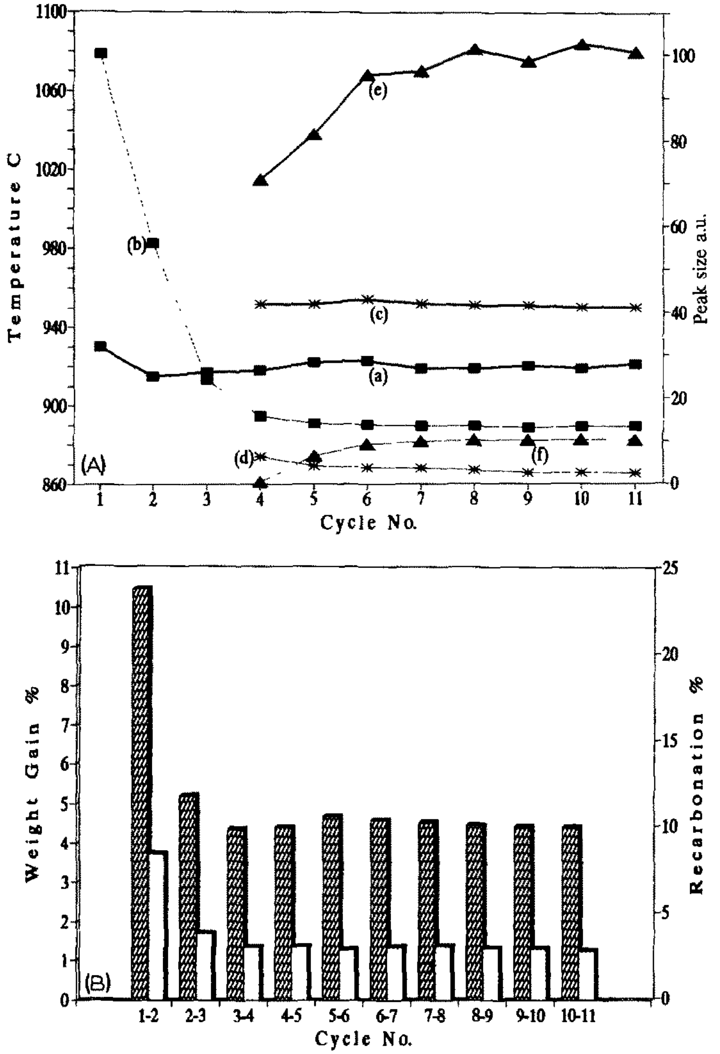

Fig. 7. Legend as for Fig. 5, but temperature range was 550–1270 °C (cf. Fig. 4): ■, first ((a) and (b)); *, second ((c) and (d)); ▲, third ((e) and (f)) endotherm.

endotherm extending up to the main peak. More probably, the minute endotherm is due to sintering of some of the calcite.

Recarbonation

On cooling, partial recarbonation occurred, as demonstrated by a gain in weight of the samples, associated with an exotherm. The reaction commenced abruptly and peaked at about 860–870 °C, almost independent of the heating regime. At fast heating rates (30 °C min^{-1} and above) and a maximum heating temperature of 1170 °C the degree of recarbonation was

TABLE 1

Effect of residence time at 1170 °C on subsequent cooling–heating cycles

Time at 1170 °C (min)	Cycles required for appearance of		Cycles required to reach minimum wt. gain on cooling	Wt. gain (%) on cooling	
	2nd endotherm	3rd endotherm		1st cycle	9th cycle
0	>11	≫11	10	13.40	3.22
5	6	8	7	12.22	3.16
10	6	8	6	11.46	3.40
15	4	5	3	8.96	–
90	3	4	2	6.34	–
150	3	4	2	6.20	4.90
240	3	4	2	5.96	–

reduced in successive heating–cooling cycles until a steady state was reached after the ninth cycle (Fig. 5(B)). A similar decrease in recarbonation was previously observed in isothermal experiments in which the heating cycles were carried out under N_2 and the cooling cycles under CO_2 [12]. At lower heating rates (5 °C min^{-1} or less) a different pattern was revealed; the weight gain decreased in the first three cycles, but increased beyond that until a steady state was reached after the seventh cycle. The increase in weight gain was associated with a change in configuration of the subsequent endotherm, which is discussed below (Fig. 6).

Samples heated to 1270 °C at 30 °C min^{-1} showed a rapid decrease in recarbonation after the first cycle and no substantial change in subsequent cycles (Fig. 7(B)).

Initially, recarbonation was greater with samples cycled to 1170 °C than with those heated at the same rate to 1270 °C, but when the steady state was reached samples heated to the higher temperature showed a total weight gain of about 6%, compared with only about 4% on milder treatment (Figs. 5(B) and 7(B)).

Table 1 shows the effect of varying residence times at 1170 °C preceding the cooling–heating cycles. Initially the extent of the back reaction decreased with increasing time of heating the CaO, from 13.40% to 5.96% for residence times of 0 min and 240 min respectively. However, after several cycles a change occurred: samples that were exposed to longer initial heating periods were more reactive than those that had been heated for shorter times.

Calcite that was decomposed in a CO_2-containing atmosphere produces CaO of high surface area and an essentially bimodal distribution of pores—megapores with about 1–2 μm diameter and mesopores with diameter of only 5 nm [13 and references cited therein]. Beruto et al. [13] observed a decrease in mesoporosity with heating time in CO_2; lower surface areas and mesoporosities were obtained after cooling and reheating than for samples heated for the same total time at the maximum temperature of the experiment. They inferred that thermal cycling caused closer repacking of CaO rods. It is well established that CO_2 catalyses sintering of CaO [5]. Apparently in the present experiments, sintering caused by lower heating rates, by more prolonged heating at 1170 ° C or by heating to a higher temperature (1270 ° C) decreased the initial surface area of the CaO, but also reduced the ability of the rods to reorient in subsequent thermal cycles, thus preserving a higher mesoporosity.

Scanning electron micrographs of recarbonated samples heated to 1170 ° C are indistinguishable from those heated to 1270 ° C. The particles are strongly fractured, showing elongated, almost parallel rifts. The outline of the original particles can sometimes be discerned, usually showing a central cavity of about 1–2 μm in diameter (Fig. 1(c), centre). The particles are sintered and tend to intergrow. This tendency increases in subsequent heating cycles, but the morphology does not change substantially, even after the most prolonged heat treatment followed by 30 heating and cooling cycles (Fig. 1(d)). Occasionally odd shapes result (Fig. 1(e)).

An additional feature that appeared on the cooling curves in the first few cycles is a small upward kink on the low temperature side of the exotherm without a corresponding break in the TG or DTG curves. This exothermic feature was entirely reproducible and was more pronounced at lower heating rates (Fig. 3). It seems probable that this reaction corresponds to recrystallisation of amorphous or poorly crystallised calcite, as previously observed on recarbonation of highly reactive CaO produced by decomposing calcite in vacuum [7]. This hypothesis receives support from XRD patterns of samples withdrawn just before and after the kink, at positions a and b in Fig. 3. The samples were rapidly quenched in CO_2 and immersed in petroleum jelly. The diffractometer traces showed that the ratio of $CaCO_3$ to CaO, based on peak areas, increased by about 50% between points a and b. Because this increase was not accompanied by a gain in weight of the sample, it is not due to recarbonation and must be attributed to recrystallisation of poorly-crystalline calcite.

During the heating cycles an additional weight gain was observed (Figs. 2–4). This commenced at about the temperature at which recarbonation ceased on cooling, owing but continued to higher temperatures than in the cooling cycles. In fact the temperature at which carbonation ceased on heating could not be established, because of overlap between the forward and back reactions. In samples heated to 1170 ° C the weight gain was sometimes associated with one or two small exotherms (Fig. 3). These are too small to account for calcite formation corresponding to the observed weight increase. Moreover, they were absent in many runs in which similar weight increases were recorded.

Previous investigators [12,14] who studied the reversibility of calcite decomposition observed an initial, fast recarbonation followed by a slower reaction. They attributed the fast component of the carbonation to a surface reaction, which is followed by a slower, diffusion-controlled reaction. It seems that the weight gains in the present experiments can be explained by a similar mechanism, the first, on cooling, owing to the formation of a surface coating and the second, on heating, to penetration of CO_2 into the interior of the particles. The fact that the second weight gain proceeds to higher temperatures than the first, with only a small or no associated exotherm, suggests that calcite formation and decomposition partially overlap. Some pores and cracks become blocked, trapping CO_2 in the process. This causes an increase in weight without an exothermic reaction. The weight gain on heating was much lower than that on cooling, but followed a similar pattern. Samples exposed to higher temperatures or more prolonged heating periods initially took up less CO_2 than those subjected to milder heat treatment, but this was reversed after several heating cycles.

Figure 1(f) shows the morphology of a sample maintained for 18 h at 880 °C during the heating cycle. Recarbonation had reached 96%. The particles were sintered and most of the cracks were healed. Crystals can be seen growing out of some of the fissures.

Decarbonation, subsequent cycles

Decarbonation, which initially occurred in a single step, became more complex in subsequent heating cycles. The course of the reactions depended on the thermal regime, one, two or three endotherms being observed (Figs. 2, 3 and 4 respectively). The first two were generally sharp peaks, the third was broad and appeared to be composite (Fig. 4). All were associated with weight losses.

A sample cycled to 1170 °C at 30 °C min^{-1} gave rise to only one endotherm throughout 10 cycles, but after several cycles this peak became asymmetrical and ultimately developed a small shoulder on the high temperature side (Fig. 2). Cycling to 1170 °C at lower heating rates gave rise to two endotherms after the third cycle (Fig. 3). Cycling at 30 °C min^{-1} up to 1270 °C produced three endotherms after only three cycles (Fig. 4). Similarly, static heating at 1170 °C before cycling led to two or three endotherms. The longer the residence time at the high temperature, the fewer the cycles required for the appearance of the second and third endotherms (Table 1).

The complexity of the endothermic reaction may be interpreted as follows. In the process of heating the sample, CO_2 diffuses into the interior of the particles. In part it reacts to form calcite and in part it is trapped in closed pores, as discussed above. As the temperature is raised the pressure in the pores increases and the equilibrium of reaction (1) is shifted to the left in an exothermic reaction. This process is superimposed on the decomposition of calcite at ambient pressure. Owing to the smaller crystallite size of the recarbonated phase, decomposition generally commenced at a lower temperature than with the original sample. Again, departure from the baseline was abrupt.

It seems that the number of endotherms observed depends on the balance between the mesoporosity and macroporosity of the samples. When the sample was cycled rapidly to 1170 °C, the exotherm due to the reaction between CaO and CO_2 diffusing into the particles on heating exactly overlapped the endotherm. The pores were not blocked and calcite decomposition occurred under ambient conditions. The slight asymmetry indicates a minor displacement of the exotherm relative to the endotherm.

On slower heating, two endotherms appeared after the third cycle, when recarbonation had reached a minimum value (Fig. 5). Both features probably reflect a change in the distribution of mesopores and macropores. This phenomenon merits more detailed study.

On cycling to 1270 °C, or after various residence times at 1170 °C and subsequent cycling, three endotherms appeared. Evidently the CaO was more sintered and some mesopores, in which CO_2 was trapped, remained sealed to higher temperatures. Because CO_2 was trapped over a range of temperatures, the pressure in the pores differed. As the temperature was raised, additional calcite was formed inside the pores and, simultaneously, some pores were unblocked and exposed to ambient pressures. Calcite was thus progressively decomposed, in amounts exceeding those of calcite formed. This accounts for the gradual weight loss and for the width and asymmetry of the third endotherm. The shape of this peak contrasts sharply with that of the two narrow lower temperature peaks (Fig. 4).

SUMMARY AND CONCLUSIONS

A sample of calcite was subjected to repeated heating and cooling cycles under constant CO_2 pressure. The only variable was the heating regime. The morphology of the samples, as revealed by scanning electron microscopy, was changed profoundly in a single heating cycle, whatever the heating regime. Subsequent cycles or prolonged heating at high temperature, i.e. after decarbonation, had a relatively minor effect on the morphology. In contrast, DTA/TG/DTG curves of samples exposed to various heat treatments differed greatly. It appears that the thermal characteristics are largely determined by the mesoporosity of the samples, which is beyond the detection limit of the scanning electron microscope.

Decomposition of the original sample gave rise to a single sharp endotherm, with a peak at 900–940 °C, depending on the heating rate. This was occasionally preceded by a small endotherm, perhaps due to sintering of some of the calcite before decomposition. On cooling, recarbonation occurred accompanied by an exothermic peak at 860–870 °C. This temperature was almost independent of the heating regime, but the degree of recarbonation differed. An additional, small exotherm which sometimes occurred was attributed to recrystallisation of poorly crystallised calcium carbonate.

During subsequent heating cycles, an initial weight gain was followed by a weight loss. A small exotherm was occasionally observed and, depending on the heating regime, one, two or three endotherms. The peak temperature of the first was generally lower than that of the original calcite, probably due to smaller particle size. The third endotherm was always broad and the peak temperature frequently exceeded 1100 ° C.

The following reaction scheme is proposed. On cooling after decarbonation, recarbonation of the surfaces occurs rapidly, with little diffusion into the inside of the particles. On subsequent heating CO_2 penetrates into the inside of the particles, some is trapped and formation of calcite in closed pores overlaps with decomposition at ambient pressure. The balance between these opposing processes apparently depends on the distribution of megapores and mesopores in the CaO and on the ability of the newly-formed $CaCO_3$ and sintered CaO to block mesopores, thus preventing escape of trapped CO_2. With increasing temperature the pressure inside the pores rises. Some burst, releasing CO_2 and exposing more calcite to ambient pressures, in others, which remain blocked, more calcite is formed. These processes are reflected in the various configurations of the decomposition endotherms and in the corresponding weight loss curves. A high temperature phase transition of calcite may be involved, but could not be confirmed. Similarly if recrystallisation of reactive CaO occurred, this would have been obscured by other reactions.

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