Thermochimica Acta, 165 (1990) 281–296
Elsevier Science Publishers B.V., Amsterdam

THE THERMAL DECOMPOSITION OF DOLOMITE

R.M. McINTOSH, J.H. SHARP and F.W. WILBURN

School of Materials, Division of Ceramics, Glasses and Polymers, University of Sheffield, Sheffield S10 2TZ (Gt. Britain)

(Received 26 January 1990)

ABSTRACT

The thermal decomposition of dolomite, $CaMg(CO_3)_2$, has been studied by obtaining thermogravimetric and differential thermal analysis curves in various controlled atmospheres involving the use of N_2–CO_2 mixtures. The DTG and DTA curves show two peaks: the first is associated with the formation of magnesia and calcite, the second with the decomposition of this calcite. The temperature of the second peak increases with increasing partial pressure of carbon dioxide, but the first peak behaves in an anomalous manner. At first it decreases in temperature with increasing partial pressure of carbon dioxide, reaching a minimum value between 10% and 20% carbon dioxide. Subsequently it increases, although the temperature at 1 atm of carbon dioxide is still below that in 1 atm of nitrogen. The addition of either ammonium chloride or sodium carbonate reduces the decomposition temperature of the first peak, liberating magnesite. It is proposed that the mechanism of the decomposition of dolomite is via the formation of the two separate carbonates of magnesium and calcium.

INTRODUCTION

Dolomite is the mineral form of the double carbonate of calcium and magnesium, $CaMg(CO_3)_2$. It has a similar crystal structure to that of calcite, having a face-centred rhombohedral cell [1]. It has often been assumed that on heating, dolomite decomposes in two separate stages

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad \text{(Stage 1)}$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(Stage 2)}$$

Like those of calcite and magnesite, the dolomite decomposition process has been studied extensively [2–28]. DTA curves for 100 mg samples of dolomite show two definite endothermic peaks. The lower temperature peak represents the decomposition of the dolomitic structure, releasing carbon dioxide from the carbonate ions associated with the magnesium part of the structure, accompanied by the formation of calcite and magnesium oxide. The higher temperature peak represents the decomposition of calcite with evolution of carbon dioxide.

A TG curve for dolomite shows a distinct change of slope at about 50% mass loss, thus producing two distinct peaks on a DTG curve. Wilsdorf and Haul [21] have shown that both calcite and magnesium oxide are present at this half-way stage of the decomposition.

The peak temperature of the first part of the decomposition on a DTA or DTG curve is some 100 °C higher than that obtained for the equivalent quantity of magnesite tested under similar experimental conditions. The peak temperature of the second part is similar to that expected for an equivalent amount of calcite.

On close inspection, most of the published DTA and DTG curves for dolomite actually show a lowering of the first decomposition peak temperature when the experiments are carried out in carbon dioxide atmospheres rather than in nitrogen or air. Haul and Heystek [5] and Stone [26] make no comment on this phenomenon, whilst Rowland and Lewis [4] and Hurd [9] note it without offering any explanation. In a thorough study, Bandi and Krapf [25] concluded that the commonly published curve showing two endotherms and a step-wise decomposition of dolomite is really a special condition of decomposition in which the partial pressure of carbon dioxide is greater than 200 Torr inside and/or around the dolomite sample. They state: "Even though most published literature says that the first endotherm is not sensitive to carbon dioxide pressure and the second endotherm is, the present experiments prove that both endotherms are sensitive to carbon dioxide pressure but in opposite ways".

There is even greater uncertainty about the mechanism of the thermal decomposition, especially that of the first stage. In view of these uncertainties, it seemed timely to analyse in detail the temperature variation shown in the thermal analysis curves obtained in controlled atmospheres. The results are considered in the light of the various ideas that have been postulated to explain the decomposition reactions.

EXPERIMENTAL

The thermobalance used for these studies was a Stanton HT-SF type, having a full scale deflection of 20 mg with offset facility, and being capable of detecting mass changes of 0.1 mg. The furnace atmosphere was controlled by introducing the desired gas into the sample area through the top of the furnace tube, which was cooled by a water jacket. Using a flow rate of 200 ml min^{-1} of nitrogen, a sample of powdered graphite heated to 1200 °C showed no loss in mass due to oxidation. For all studies on the decomposition of dolomite a standard flow rate of 300 ml min^{-1} was used. Corrections for buoyancy effects in gaseous atmospheres were carried out by heating inert powdered alumina in the alumina crucible used for the rest of the work. These crucibles were cylindrical with vertical sides and measured 1 cm in depth by 1 cm internal diameter.

The temperature trace on the balance recorder was calibrated against a thermocouple directly beneath the sample and the corrected temperature plotted against the observed loss in mass. DTG curves were drawn from these TG curves. The temperatures of the DTG peaks are estimated to be accurate to ±5 °C.

The gas-flow system using calibrated flow meters allowed nitrogen and carbon dioxide to be mixed in the correct proportions and dried using silica gel and magnesium perchlorate contained in two U-tubes. A third U-tube containing a molecular sieve was used to remove traces of carbon dioxide from the nitrogen. A conical flask containing distilled water and fitted with a sintered glass bubbler enabled the gas being used to be saturated with water vapour at ambient temperature. Similar systems were used with both the thermobalance and the DTA apparatus.

The quantitative DTA cell designed by Wilburn [29] was considered ideal for the studies reported here. The cell was adapted for use in controlled atmospheres. The cylindrical high-conductivity nickel block has two cylindrical sample wells, each lined with a silica sheath. Chromel–alumel thermocouples were used for temperature measurement and were located vertically in the lower part of the sample wells. Sample holders which were made from 0.001 in platinum sheet fit snugly into the silica sheaths and rest on the exposed beads of the measuring thermocouples. A sample mass of 100 mg was used in the DTA experiments.

The most suitable heating rate available on the Stanton thermobalance for TG experiments was 7 °C min^{-1} compared to the 10 °C min^{-1} used for DTA experiments. It was found that more useful information could often be gained using the much slower heating rate of 1 °C min^{-1}. In addition isothermal experiments were carried out at suitable pre-determined temperatures.

RESULTS

Dynamic thermal methods

Samples of dolomite (200 mg) were heated on the thermobalance at 7 °C min^{-1} in various carbon dioxide/nitrogen atmospheres. The results are given in Table 1. The temperature of the first DTG decomposition peak for a sample run in a 10% CO_2 partial pressure gas mixture was found to be 37 °C lower than a similar run in pure nitrogen, although the peak temperature of the second decomposition was 12 °C higher in the 10% CO_2/N_2 mixture as might be expected. Further experiments, using various carbon dioxide partial pressures, showed that the first decomposition peak tempera-

TABLE 1

The effect of atmosphere on the DTG peak temperatures of dolomite

Atmosphere	First peak (°C)			Second peak (°C)		
	DTG ($1^\circ C$ min^{-1})	DTG ($7^\circ C$ min^{-1})	DTA ($10^\circ C$ min^{-1})	DTG ($1^\circ C$ min^{-1})	DTG ($7^\circ C$ min^{-1})	DTA ($10^\circ C$ min^{-1})
N_2	745	807	802	805	875	882
N_2-5%CO_2	–	787	–	–	885	–
N_2-7.5%CO_2	–	782	–	–	895	–
N_2-10%CO_2	720	770	780	830	887	885
N_2-20%CO_2	695	777	768	830	910	892
N_2-30%CO_2	705	–	772	848	–	902
CO_2 (100%)	730	790	773	925	955	943

ture was at its minimum value for about 10% CO_2 partial pressure. The first decomposition peak temperatures were lower for all partial pressures of carbon dioxide (with $P_{total} = 1$ atm) than those in nitrogen. The second decomposition DTG peak temperatures generally increased with increasing carbon dioxide partial pressure, although the peak temperature for the second decomposition peak in 10% CO_2 partial pressure was lower than that for 7.5% CO_2 partial pressure. Apart from this anomaly the second decomposition peak temperatures occur at approximately those temperatures expected for a similar mass of calcite in these atmospheres.

To investigate these decompositions further, additional TG curves were obtained at the very slow heating rate of 1° C min^{-1}; these curves showed similar but more marked effects, as shown in Fig. 1 where α, the fraction reacted, is plotted against temperature. It can be seen that the plateau in

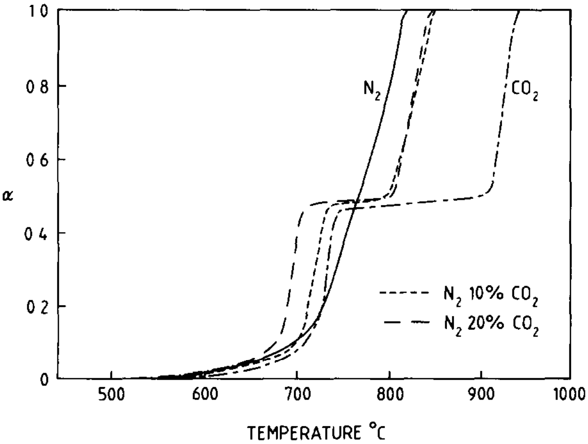

Fig. 1. TG curves for dolomite heated at 1° C min^{-1} in various atmospheres. α = fraction reacted.

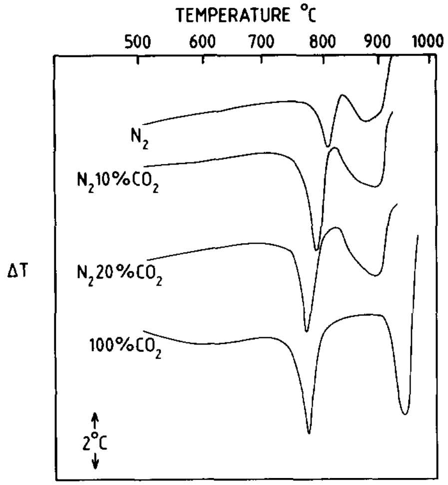

Fig. 2. DTA curves for dolomite heated at 10 °C min^{-1} in various atmospheres.

these curves during which little loss in mass occurred was most pronounced in an atmosphere of 100% CO_2. It became only a kink in the curve obtained in 100% N_2 at 1 °C min^{-1}, but showed a clear inflection at $\alpha \approx 0.5$ when heated at 7 °C min^{-1}. That part of the TG curve in 100% N_2 in the range $0.2 < \alpha < 0.5$ is at the highest temperature, whereas that part at $\alpha > 0.5$ is at the lowest temperature.

The DTA curves shown in Fig. 2, obtained at 10 °C min^{-1}, and the data given in Table 1 based on these DTA curves, together with the DTG curves obtained at 1 °C min^{-1}, provide additional confirmation of the anomaly. The peak temperature associated with the first stage of the decomposition decreased with increasing partial pressure of carbon dioxide until it reached a minimum in atmospheres containing 20% carbon dioxide. As the partial pressure of carbon dioxide was increased further the peak temperature increased, but peak temperatures for all carbon-dioxide-containing atmospheres were lower than those for the corresponding runs in nitrogen. Strictly it would be more correct to compare onset or extrapolated onset temperatures from these DTA curves rather than peak temperatures. The latter are, however, easier to determine. Estimates of the extrapolated onset temperatures indicate that the anomaly is even greater when these are compared than when peak temperatures are compared. The second decomposition peak temperature increased with increasing partial pressure of CO_2 from both DTG and DTA. The TG results at 1 °C min^{-1} showed an apparent arrest in the increase of the second decomposition peak temperature, as shown by DTG, in the region of CO_2 partial pressures which gives the lowest first decomposition temperatures.

The DTA peak temperatures obtained at 10 °C min^{-1} on 100 mg samples are similar to the DTG peak temperatures obtained at 7 °C min^{-1} on 300

TABLE 2

Separation of the two peaks as determined by thermal analysis

Atmosphere	DTG ($1^\circ C\ min^{-1}$) (°C)	DTG ($7^\circ C\ min^{-1}$) (°C)	DTA ($10^\circ C\ min^{-1}$) (°C)
N_2	60	68	80
5% CO_2	–	98	–
7.5% CO_2	–	113	–
10% CO_2	110	117	105
20% CO_2	135	133	124
30% CO_2	143	–	130
100% CO_2	195	165	170

mg samples (Table 1), but, as expected, are much higher than those at 1° C min^{-1}. Our TG curve at 1° C min^{-1} in 100% CO_2, however, agrees well with that published recently by Engler et al. [19] on a 95 mg sample heated at 3° C min^{-1} in a carbon dioxide atmosphere.

As the partial pressure of CO_2 was increased, the separation of the two peaks on the DTG and DTA curves was found to increase (Table 2) and the peaks became sharper. The separation is seen to depend upon the partial pressure of carbon dioxide, whereas variation in other procedural variables, such as heating rate and sample mass, has little effect. The data of Engler et al. [19] again confirm this observation; they heated 95 mg samples on a thermobalance at 3° C min^{-1} in CO_2 and obtained a separation of the two peaks of about 200° C. Similarly, Stone [26], using DTA, reported a separation of only 65° C in nitrogen but of 160° C in CO_2.

The DTG curves at 1° C min^{-1} show that, for all except the run in nitrogen, the resolution of the two peaks is complete. Closer examination of the TG curves at 1° C min^{-1} (Fig. 1) shows that the curve obtained in a nitrogen atmosphere follows a different path from those taken in carbon dioxide atmospheres. The initial reaction is as rapid in nitrogen as in the lower partial pressures of carbon dioxide, and faster than in the higher partial pressures of carbon dioxide. Between 660° C and 700° C however, the rate of reaction in carbon dioxide rapidly increases, overtaking the rate of decomposition in nitrogen, where the increase in rate is delayed until above 700° C. This suggests that a different kinetic mechanism is operating in an atmosphere of nitrogen from that in carbon dioxide.

Isothermal experiments

To test this hypothesis, a series of isothermal mass-loss experiments at various temperatures, both in nitrogen and 10% CO_2/90% N_2 mixture were carried out, and typical curves are reproduced in Fig. 3. The shapes of the

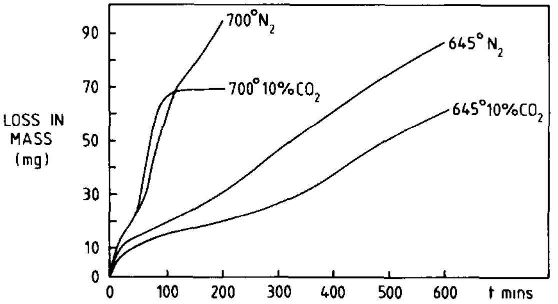

Fig. 3. Isothermal gravimetric curves for the decomposition of dolomite in N_2 and N_2–10% CO_2 atmospheres at 645 and 700 ° C.

curves for the higher temperature set of isothermal experiments (700 ° C) are different from those at 645 ° C. In these latter curves the initial rate of reaction was much slower in 10% CO_2 partial pressure, but at about 40% reaction, the rate increased to become comparable with that of the experiment in nitrogen. At 700 ° C, however, the curve obtained in 10% CO_2 is initially almost superimposed on that obtained in nitrogen, but showed a more rapid reaction above 30% reaction. Thus a different kinetic mechanism must be operating at these higher temperatures.

A plot [30] of fraction reacted against reduced time, $t/t_{0.5}$, shows that the experiment carried out in nitrogen at 645 ° C gives an approximately straight line (Fig. 4), indicative of zero-order kinetics. A similar plot of the data obtained in 10% CO_2 at 645 ° C, on the other hand, shows definite sigmoidal characteristics. Similar sigmoidal curves were also observed at higher temperatures in both atmospheres, such as that obtained in 10% CO_2 at 700 ° C shown in Fig. 4; this characteristic was most pronounced at higher temperatures in 10% CO_2. It seems that the curves obtained from the TG experiments in 10%–20% CO_2 initially show the characteristics of the low temperature isothermal curves and subsequently those of the higher temperature isothermal curves. These observations confirm the complexity of the kinetic mechanisms in the various partial pressures of carbon dioxide.

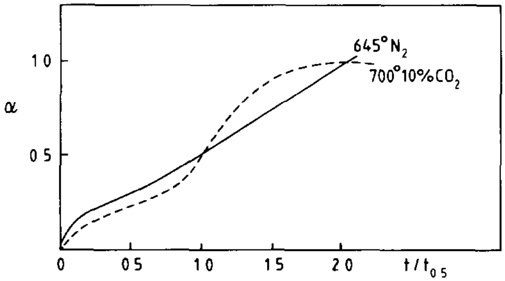

Fig. 4. Reduced time plots of the fraction reacted, α, against $t/t_{0.5}$ for two isothermal experiments.

DISCUSSION

Relationship to other published work

Numerous other workers have made similar observations to those reported here and the results are summarised in Table 3. These workers have, however, either disregarded the results or claimed that the first stage of the decomposition of dolomite occurs at the same temperature in air (or nitrogen) and in carbon dioxide, even when their own published curves show a definite reduction in the decomposition peak temperature in CO_2.

Some previous workers have used reduced pressures of carbon dioxide, but of those that have worked at 1 atm total pressure, only Bandi and Krapf [25] have used atmospheres other than air, nitrogen or 100% carbon dioxide. The present study not only confirms their conclusion that the peak temperature of the first stage of the decomposition can be reduced in temperature, but that it varies in a complex manner dependent on the partial pressure of carbon dioxide. The minimum peak temperature also depends on other procedural variables, such as the heating rate and sample mass, because these in turn influence the actual atmosphere around the decomposing sample.

TABLE 3

Comparison of results from different literature references

Reference	Gas	DTA (°C)		DTG (°C)	
		1st	2nd	1st	2nd
4	Air	820	920		
	CO_2	790	940		
23	Air	805	920		
	CO_2	790	940		
5	Air	825	945		
	CO_2	810	975		
26	N_2	805	870		
	CO_2	775	935		
9	N_2			790	830
	CO_2			770	925
This work	N_2	802	882	807	875
	CO_2	773	943	790	955

Reaction mechanism

The first stage of the decomposition can be represented overall by the equation

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \tag{1}$$

but Hashimoto et al. [27] and Otsuka [18] have indicated that this involves either (i) primary dissociation into oxides followed by recarbonation or (ii) direct formation of calcium carbonate. The first mechanism may involve an exchange reaction with unreacted dolomite

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \tag{2}$$

$$CaO + CaMg(CO_3)_2 \rightarrow MgO + 2CaCO_3 \tag{3}$$

or recarbonation by reaction with the carbon dioxide in the atmosphere

$$CaO + CO_2 \rightleftharpoons CaCO_3 \tag{4}$$

The second mechanism may proceed via the formation of a magnesite–calcite solid solution

$$CaMg(CO_3)_2 \rightarrow CaCO_3 \cdot (1-n)MgCO_3 + nMgO + nCO_2 \tag{5}$$

where n increases from 0 to 1 with increasing time, or via primary dissociation into the two carbonates followed immediately by the decomposition of the magnesite so formed

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_3 \tag{6}$$

$$MgCO_3 \rightarrow MgO + CO_2 \tag{7}$$

It has been shown by other workers, e.g. Wilsdorf and Haul [21], that after the first stage of the dolomite decomposition the calcium is entirely present as calcite, and moreover that the reaction is topotactic, i.e. the calcite is formed with definite orientation relations to that of the original dolomite. If the dolomite decomposed into its constituent oxides (mechanism (i)), it would lose 47.73% of its original mass and the large molecule (CO_2) being evolved would be expected to disrupt the crystal leading to a reaction product with random orientation. The observed topotaxy is evidence in favour of the second mechanism which allows the carbonate framework to remain intact whilst the calcite is formed from the dolomite by counter-migration of Ca^{2+} and Mg^{2+} ions.

Hashimoto et al. [27] concluded that the mechanism of the reaction involved the direct formation of calcium carbonate via magnesian calcite with a gradual release of Mg^{2+} ions to form calcite. They suggested that the evolution of carbon dioxide from surface defects initiates decomposition, rather than dissociation into the two carbonates as in eqn. (6). Although this theory is very attractive and explains many features of the decomposition, it is not clear why the decomposition temperature should increase with decreasing partial pressure of carbon dioxide.

The evidence sometimes cited for the alternative mechanism, based on the primary dissociation into oxides as in reaction (2), is that very small samples of dolomite only give a single DTA or DTG peak, as also do samples heated in vacuo [25]. We believe that this can be attributed to the expected variation in decomposition temperature of calcite with sample size, and is not contrary to the second mechanism. For example, the DTA peak temperature for a 1 g sample of calcite is about 900 °C (as obtained on early DTA equipment), some 300 °C higher than that expected from a 2 mg sample (as used in some modern DTA equipment). The large sample generates its own atmosphere of carbon dioxide, as discussed by Bandi and Krapf [25], and the decomposition of calcite obeys the laws of thermodynamics, according to the temperature and partial pressure of carbon dioxide. A small sample, without this back pressure of carbon dioxide, gives rise to a single DTA peak involving the decomposition of both carbonates in the same temperature range.

Berg [31] has shown that under very high carbon dioxide pressures (90–100 atm) the DTA curve for dolomite shows a small endotherm at 750 °C, which he ascribes to the dissociation of dolomite into the separate carbonates, reaction (6), which would require only a small heat of reaction (≈ 6.5 kJ mol^{-1}). This is followed by a large endothermic peak at 850 °C which Berg attributes to the decomposition of the magnesium carbonate. This temperature corresponds with that expected for the dissociation of magnesium carbonate calculated from thermodynamic considerations at these pressures. Berg concluded that under normal atmospheric pressure the dissociation pressure of magnesium carbonate exceeds 1000 Torr at the dolomite decomposition temperature. Therefore, when the magnesium carbonate is released it is thermodynamically unstable and thus decomposes instantaneously and is not affected by the external carbon dioxide pressure.

Haul and Heystek [5] had previously suggested that over the temperature range of the first stage of the dolomite decomposition, the theoretical dissociation pressure far exceeds the carbon dioxide pressure around the sample. Hence the temperature at which the decomposition occurs exceeds the thermodynamic decomposition temperature. The dissociation is, therefore, expected to take place over a narrow temperature range. This theory in effect supports the second mechanism, including eqn. (6).

The major difficulty with this mechanism is that Engler et al. [19] did not observe the intermediate formation of magnesium carbonate in their recent X-ray diffraction study. If, however, magnesium carbonate is formed above 650 °C, its presence would be very transient because of its rapid dissociation into magnesia. Furthermore, it would probably be poorly crystalline and might not be readily detected by X-ray diffraction. Nor did Engler et al. [19] detect the intermediate formation of calcium oxide, although one or other intermediate phase seems to be necessary on mechanistic grounds.

A possible explanation of the observed anomaly is that a secondary kinetic effect is superimposed on the expected thermodynamic control of the reaction through the second mechanism. Thermodynamic considerations determine the temperature at which magnesite and calcite are formed in reaction (6). The calcite can be formed with good orientation relations to the original dolomite and is below its decomposition temperature in carbon-dioxide-containing atmospheres. The magnesite, on the other hand, is well above its thermodynamic decomposition temperature at the carbon dioxide pressures investigated, and hence starts to decompose immediately it is liberated. The rate of this decomposition is dependent on kinetic factors influencing the nucleation and growth of magnesia crystallites. Such factors include the exchange of carbon dioxide [24,25,32] and the presence of dislocations [33].

To investigate this hypothesis further, two more sets of experiments were carried out. First, we examined the influence of incorporating water vapour in the ambient atmosphere on the decomposition of dolomite. Second, to extend the studies of Webb and Kruger [34] and Bandi and Krapf [25] who added sodium chloride to dolomite, we have investigated additions of ammonium chloride and sodium carbonate.

EFFECT OF WATER VAPOUR

TG and DTA curves were obtained on calcite and magnesite samples heated in dry atmospheres (N_2 and CO_2) and in the same atmospheres saturated with water vapour. The decomposition peaks of calcite and magnesite occurred at lower temperatures in the wet nitrogen atmospheres, while in wet carbon dioxide the decomposition peak of calcite was unchanged but that of magnesite was reduced in temperature (Table 4).

In contrast, DTA curves of dolomite in wet carbon dioxide atmospheres showed an increase in peak temperature compared with the corresponding dry atmospheres for both stages of the decomposition: the first peak by 15–20 °C, the second by 2–8 °C (Table 5). Samples heated in wet carbon

TABLE 4

Effect of water vapour on magnesite and calcite decomposition in nitrogen and carbon dioxide atmospheres

Atmosphere	Magnesite		Calcite	
	DTG (°C)	DTA	DTG (°C)	DTA
Dry N_2	645	642	910	895
N_2 sat. with H_2O	625	632	895	885
Dry CO_2		660		957
CO_2 sat. with H_2O		653		955

TABLE 5

Effect of water vapour on dolomite decomposition in nitrogen and carbon dioxide atmospheres

Atmosphere	DTA (dry)		DTA (sat. water vap.)	
	1st (°C)	2nd	1st (°C)	2nd
N_2	802	882	813	875
N_2-10% CO_2	780	885	795	892
N_2-20% CO_2	768	892	788	900
N_2-30% CO_2	772	902	790	907
100% CO_2	773	943	795	945

dioxide showed surface sintering which must affect the kinetics of the reaction. The minimum peak temperature for the first stage was observed in a wet atmosphere containing about 20% CO_2, whereas the second stage showed an increasing peak temperature with increasing partial pressure of carbon dioxide.

DTA curves for dolomite heated in a wet atmosphere of nitrogen showed that the peak temperature of the first stage increased slightly whereas that of the second stage decreased, compared with the run in dry nitrogen (Table 5).

Various authors have discussed the phenomenon of carbon dioxide exchange and its possible influence on the reaction mechanism [25]. Water vapour, when present, competes with the carbon dioxide for exchange sites and hence affects the reaction rate in the early stages. The crystallite sizes of samples taken from experiments arrested after the first decomposition peak were larger than similar samples taken from dry runs. The effect of water vapour on the crystallite growth of magnesium oxide together with the surface sintering observed on complete decomposition may account for the higher second decomposition peak temperatures recorded.

It is clear that the addition of water vapour to the system modifies the rates of reaction in various atmospheres, by bringing about different crystal growth and sintering behaviour. It is also reasonable to suggest that the use of partial atmospheres of carbon dioxide affects the kinetics of the reaction in a complex manner.

EFFECT OF ADDITIONS OF INORGANIC SALTS

Bandi and Krapf [25] and Webb and Kruger [34] discuss the effect of minor additions of sodium chloride to dolomite, which also brings about a dramatic reduction in the peak temperature of the first stage of the decomposition. In the present studies additions of larger amounts of ammonium chloride and sodium carbonate to dolomite were investigated as part of a

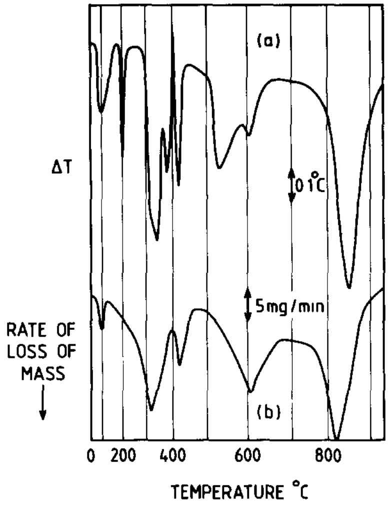

Fig. 5. (a) DTA and (b) DTG curves for a 0.67 : 1.00 mixture of ammonium chloride and dolomite.

study of glass-forming reactions [29] using a Roberts-type DTA cell [35] and a heating rate of 10 °C min^{-1}.

The DTA and DTG curves for a mixture of ammonium chloride and dolomite in a molar ratio of 0.67 to 1 are shown in Fig. 5. The peaks observed below 500 °C are all attributable to ammonium chloride, whilst those at 610 °C and 820 °C are due to the carbonate decompositions. The peak at 610 °C is much lower than any of those reported in Tables 1 and 3, and must be attributed to the intermediate formation and subsequent decomposition of magnesite, which is confirmed by the magnitude of the loss in mass.

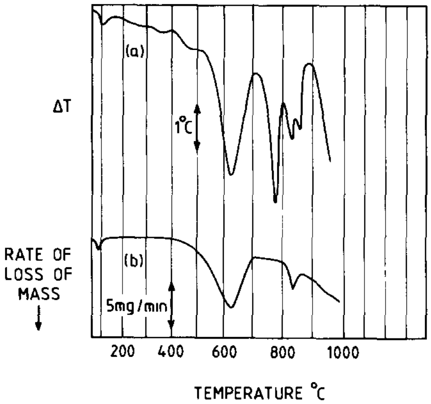

Fig. 6. (a) DTA and (b) DTG curves for a 0.64 : 1.00 mixture of sodium carbonate and dolomite.

The DTA and DTG curves for a mixture of sodium carbonate and dolomite in a molar ratio of 0.64 to 1 are shown in Fig. 6. The decomposition of magnesite can be clearly seen at 617 °C in both curves. The loss in mass associated with this peak is that expected from magnesite, but its temperature is much lower than that obtained from dolomite heated alone, even at a relatively fast heating rate on a massive sample of about 1 g. The peaks above 700 °C in Fig. 6 are all associated with melting and decomposition of the sodium calcium double carbonate formed in the reaction, or the calcite. The equations for these reactions are

$$CaMg(CO_3)_2 + Na_2CO_3 \rightarrow Na_2Ca(CO_3)_2 + MgCO_3 \qquad (8)$$

and

$$MgCO_3 \rightarrow MgO + CO_2 \qquad (9)$$

These experiments not only confirm the action of inorganic salts on lowering the decomposition temperature of the first stage of dolomite decomposition, but also establish that magnesite is found as a reaction intermediate prior to the formation of magnesium oxide. There is a close analogy between this mechanism and that described above in terms of eqn. (6).

CONCLUSIONS

(1) DTA and DTG curves of dolomite obtained in a range of atmospheres, but always at 1 atm total pressure, show two peaks. The first is associated with the formation of magnesia and calcite, whilst the second is associated with the decomposition of the calcite so formed.

(2) The temperature of the second peak increases with increasing partial pressure of carbon dioxide in an analogous way to that of calcite.

(3) The temperature of the first peak, on the other hand, behaves in an anomalous manner. At first its peak temperature decreases with increasing partial pressure of carbon dioxide, but it reaches a minimum value between 10% and 20% carbon dioxide partial pressure and subsequently increases, although the temperature in 1 atm of carbon dioxide is still lower than that in 1 atm of nitrogen.

The partial pressure of carbon dioxide at which the minimum is observed depends on other procedural variables, such as the heating rate and the sample mass.

(4) The presence of inorganic salt additions clearly reduces the decomposition temperature of the first stage. Magnesite is formed as an intermediate prior to the formation of magnesium oxide.

(5) All the experimental observations made during this study are explicable in terms of the dissociation of dolomite into the two separate carbonates

according to the equation

$$CaMg(CO_3)_2 \rightarrow MgCO_3 + CaCO_3$$

The magnesite is usually formed in a metastable state and immediately decomposes into magnesia. The rate of decomposition depends on kinetic factors influenced by the presence of carbon dioxide and/or water vapour in the ambient atmosphere.

(6) Although there are advantages in carrying out the thermal analysis of small samples, the above conclusions could only have been reached by the investigation of relatively large samples.

ACKNOWLEDGEMENT

We wish to thank Pilkington Brothers PLC for granting leave of absence to RMM.

REFERENCES

1 W.A. Deer, R.A. Howie and J. Zussman, Rock-Forming Minerals, Vol. 5, Longmans, London, 1962.
2 L.G. Berg, Dokl. Acad. Nauk SSSR, 38 (1943) 24.
3 G.T. Faust, Econ. Geol., 39 (1944) 142.
4 R.A. Rowland and D.R. Lewis, Am. Mineral., 36 (1951) 80.
5 R.A.W. Haul and H. Heystek, Am. Mineral., 37 (1952) 166.
6 W.F. Bradley, J.F. Burst and D.L. Graf, Am. Mineral., 38 (1953) 207.
7 R.L. Stone, J. Am. Ceram. Soc., 37 (1954) 46.
8 T.L. Webb, D.Sc. Thesis, Univ. of Pretoria, South Africa, 1958.
9 B.G. Hurd, Anal. Chem., 35 (1963) 1468.
10 C.W. Beck, Thesis, Harvard University, U.S.A., 1946.
11 J.L. Kulp, P. Kent and P.F. Kerr, Am. Mineral. 36 (1951) 643.
12 A.F. Gill, Can. J. Res., 10 (1934) 703.
13 M. Gibaud and M. Geloso, Chim. Anal., 36 (1954) 153.
14 K. Muraishi, Yamagata. Daigaku. Kiya. Shizein. Kagaku., 6 (1964) 187.
15 R.M. Gruver, J. Am. Ceram. Soc., 33 (1950) 96.
16 Y. Schwob, Compt. Rend. Acad. Sci., 224 (1947) 47.
17 J.A. Murray, H.C. Fisher and R.W. Shade, Proc. Natl. Lime Assoc., 49 (1951) 95.
18 R. Otsuka, Thermochim. Acta, 100 (1986) 69.
19 P. Engler, M.W. Sautana, M.L. Mittleman and D. Balazs, Thermochim. Acta, 130 (1988) 309.
20 J.V. Dubrawski and S.St. Warne, Thermochim. Acta, 135 (1988) 225.
21 H.G.F. Wilsdorf and R.A.W. Haul, Nature, 167 (1951) 945.
22 T.L. Webb and H. Heystek, in R.C. Mackenzie (Ed.), DTA of Clays, Mineralogical Soc., London, 1957.
23 R.A. Rowland and C.W. Beck, Am. Mineral., 37 (1952) 76.
24 J.L. Martin Vivaldi, F. Girela and J. Linares, Acta. Crystallogr., A25 (1969) S231.
25 W.R. Bandi and G. Krapf, Thermochim. Acta, 14 (1976) 221.

26 R.L. Stone, Anal. Chem., 32 (1960) 1582.
27 H. Hashimoto, E. Komaki, F. Hayashi and U. Uematsu, J. Solid State Chem., 33 (1980) 181.
28 L.G. Berg and V.P. Kovrzina, Zh. Neorg. Khim., 12 (1967) 569.
29 F.W. Wilburn, Ph.D. Thesis, University of Salford, 1972.
30 J.H. Sharp, G.W. Brindley and B.N. Narahari Achar, J. Am. Ceram. Soc., 49 (1966) 379; J.H. Sharp, A Citation Classics Commentary, Current Contents, 10 (1989) 13.
31 L.G. Berg, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, London, 1970, p. 354.
32 R.A.W. Haul, L.H. Stein and J.D. Louw, Nature, 167 (1951) 241.
33 J.M. Thomas and G.D. Renshaw, J. Chem. Soc. A, (1967) 2058.
34 T.L. Webb and J.E. Kruger, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol. 1, Academic Press, London 1970, pp. 321–323.
35 F.W. Wilburn, J. Soc. Glass Technol., 38 (1958) 371–382(T).