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Partial Decomposition of Dolomite in CO_2

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Thermal decomposition of dolomite into $CaCO_3$ and MgO under CO_2 was investigated by isothermal kinetic measurements, X-ray diffraction analysis, and electron diffraction. The decomposition was described as an interfacial reaction. Crystalline $CaCO_3$ is formed in an extremely orientated state even if the temperature is higher than the decomposition temperature of calcite, at least at the earlier stage of the decomposition. The crystallites of MgO grow with time and temperature, while the grain size of $CaCO_3$ remains constant during the isothermal decomposition. The $CaCO_3$ crystallite size is minimal at about 750°C. The classical theories of the mechanism of the formation of $CaCO_3$ from dolomite were reexamined, and a direct formation theory was suggested on the basis of the results of X-ray analysis.

Introduction

Certain facts have been widely recognized about the thermal decomposition of dolomite: in a vacuum, MgO and CaO are produced simultaneously, while under pressures of CO_2, $CaCO_3$ and MgO are formed at certain temperatures lower than the decomposition temperature of calcite under the given partial pressure of CO_2.

Mechanisms suggested for the formation of $CaCO_3$ have been summarized by Lange and Roesky (*1*) in the following three groups.

1. Dissociation into two carbonates and successive decomposition of $MgCO_3$ (*2*):

$$MgCa(CO_3)_2 \rightarrow CaCO_3 + MgCO_3 \rightarrow CaCO_3 + MgO + CO_2. \quad (1)$$

2. Intermediate formation of solid solution (*3*):

$$MgCa(CO_3)_2 \rightarrow CaCO_3(1 - n)MgCO_3 + nMgO + nCO_2. \quad (2)$$

n increases from 0 to 1 with time.

3a. Primary formation of oxides and successive recarbonization (*4–6*):

$$MgCa(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \rightarrow CaCO_3 + MgO + CO_2. \quad (3a)$$

3b. Primary formation of oxides and successive exchange reaction in the solid state (*7*):

$$CaO + MgCa(CO_3)_2 \rightarrow 2CaCO_3 + MgO. \quad (3b)$$

Wilsdorf and Haul (*8*) suggested a direct formation of $CaCO_3$ in the parent lattice on the basis of the X-ray analysis of the calcined single crystals of dolomite, where a high orientation of $CaCO_3$ crystallites was observed. They also carried out a tracer work (*9*) with ^{13}C. $CaCO_3$ formed by the calcination of dolomite in $^{13}CO_2$ contained much more ^{13}C than the $CaCO_3$ which was heated in $^{13}CO_2$ after its formation in normal CO_2. They considered this result not to contradict the direct formation mechanism, as the carbonate must be more active to

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exchange CO_2 with the gaseous phase during its formation than after the completion of its crystallization.

Later, Lange and Roesky (*1*) reexamined the decomposition process by high-temperature X-ray diffraction techniques, and concluded that the recarbonization mechanism, instead of the direct formation mechanism, is valid. They suggested that the results of the tracer work by Haul *et al.* (*9*) are more reasonable for the recarbonization process.

In this paper, a direct formation mechanism is again favored on the basis of the results of X-ray analysis and of electron diffraction.

Experimental

Materials. Transparent dolomite crystal (from Shibata, Japan) was powdered to an average size of about 5 μm. The relative contents of metal ions, measured by a fluorescent X-ray method, were Mg/Ca/Fe/Mn = 7.0/6.1/1.0/1.0. Other impurities, Zn, Pb, Sr, Y, Al, and P were present at concentrations of less than 0.1% of Ca. The X-ray diffraction pattern showed only the dolomite phase.

Procedure of kinetic measurements. The main part of the apparatus is illustrated in Fig. 1. A platinum crucible containing a sample of about 100 mg was brought to the bottom of the reaction tube (R), which was already heated at a constant temperature and held at a constant pressure of CO_2 by connection with a large bulb (B), 10 liters in volume.

The liberated CO_2 from dolomite was introduced into the burette (A) for a constant period, e.g., 0.5 min, successively. The burette is about 10 ml in volume and contains vacuum pump oil. The fraction decomposed (α) was calculated from the summation of the volume of the accumulated CO_2 in the burette during each period, throughout the decomposition course, and the weight loss of sample. The pressure rise of CO_2 in the burette during the accumulation was neglected because it did not exceed 1%.

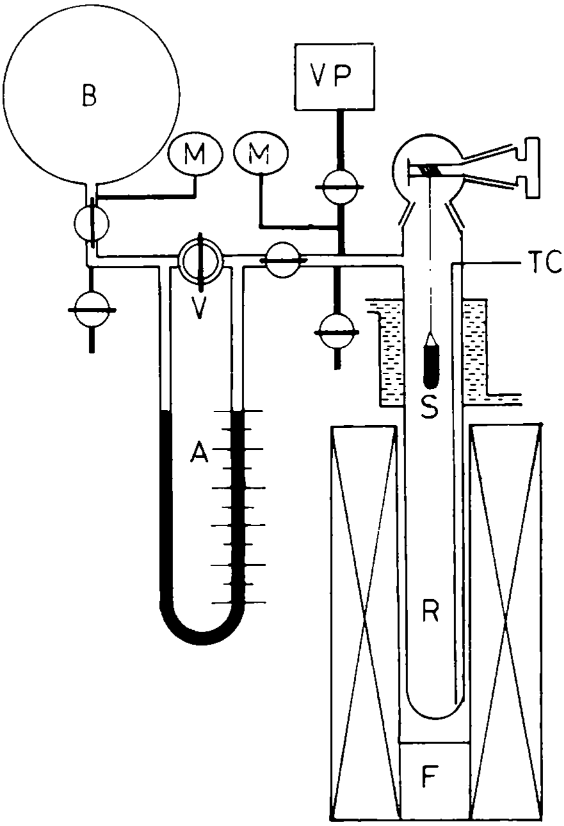

FIG. 1. Apparatus for kinetic measurement. A, burette; B, bulb; F, furnace; M, manometer; R, reaction tube; S, sample; TC, thermocouple; VP, vacuum pump; V, cock.

X-Ray analysis and electron diffraction. Ni-filtered Cu*K*α radiation was used. The following diffraction lines were selected for identification of products and also for the evaluation of grain sizes of crystallites: dolomite (104), $CaCO_3$ (104), MgO (220), and CaO (200). Although the (200) line of CaO and the (110) line of dolomite appear at the same Bragg angle, the latter did not obscure the former as dolomite lines disappeared completely before the appearance of CaO. Electron diffraction patterns of the calcined particles were taken to determine the orientation of the product crystallites.

Results

Isothermal Decomposition under CO_2

Isothermal decomposition was carried out under CO_2 pressures of 20 cm Hg; at this pressure the decomposition temperature of $CaCO_3$ is 812°C (*10*). The solid products at 950°C were CaO and MgO, and no evidence of Mn- or Fe-rich phases was observed in the X-ray diffraction profiles. The final fractional weight loss $(-\Delta W_f/W_0)$ was 0.45, which is nearly equal to the theoretical value of 0.46 calculated on the basis of an assumption that both impurities, Mn and Fe, are present in solid solution, originally in the carbonate and after calcination in the oxides. The fraction decomposed, $(\Delta W/\Delta W_f)$, at any time t is denoted by α.

Isothermal curves at various temperatures are shown in Fig. 2. At temperatures lower than 812°C, dolomite decomposes into $CaCO_3$ and MgO, and the reaction rate becomes negligible when $\alpha \doteqdot 0.5$. In this case, α', twice α, may be conveniently used to express the extent of the reaction. At higher temperatures, the reaction is very rapid up to $\alpha = 0.5$, and after this point it slows markedly.

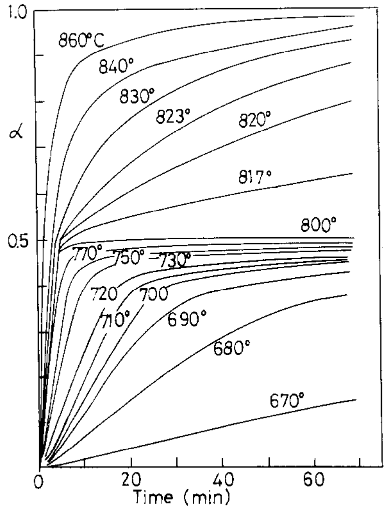

FIG. 2. Plots of fractional decomposition against time (CO_2; 20 cm Hg).

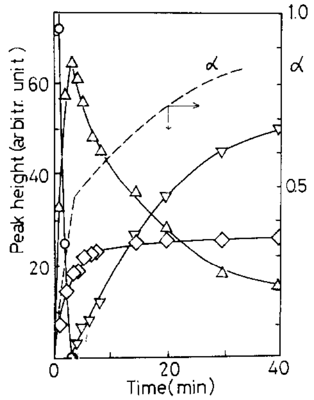

FIG. 3. Plots of peak height of X-ray diffraction from products in decomposing dolomite and fractional decomposition against time (830°C, CO_2; 20 cm Hg). ○, dolomite; △, $CaCO_3$; ◇, MgO; ▽, CaO; ---, α.

The change of the amount of each phase in the decomposing sample with time was observed by the diffraction method. Samples, heated for various times, were weighed and analyzed with X-ray diffraction. The height of the selected peak for each product and α or α' are plotted against time in Figs. 3 and 4, for the runs at 830 and 700°C, respectively. It is remarkable that a considerable amount of $CaCO_3$ is formed in the earlier stage of decomposition even at 830°C although it is theoretically unstable. At the tme that $\alpha = 0.5$, the amount of $CaCO_3$ reaches a maximum, and dolomite disappears. In order to further study this phenomenon, experiments were repeated at various temperatures under CO_2 pressures of 20, 40, 60, and 76 cm Hg, and also using another dolomite (dolomite from Akasaka, Japan, in which the Mn and Fe concentrations are less than those from Shibata). In a range of ca. 50°C above the decomposition temperatures for $CaCO_3$ under the given pressures of CO_2, the forma-

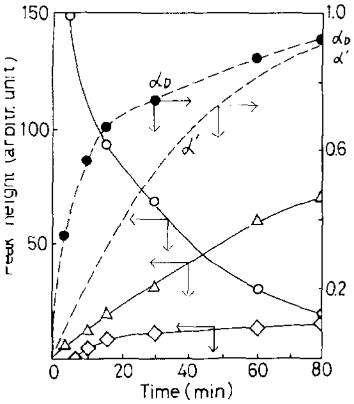

FIG. 4. Plots of X-ray diffraction peak heights from products in decomposing dolomite and fractional decomposition against time (700°C, CO_2; 20 cm Hg). ○, dolomite; △, $CaCO_3$; ◇, MgO; ●, α_D and α'.

tion of $CaCO_3$ was always observed. MgO was formed immediately after the start of heating, but CaO appeared always only after the maximum point of $CaCO_3$ formation.

Figure 4 is an example of results under conditions for which $CaCO_3$ is stable. The intensities of diffraction lines of dolomite decrease with time, but neither line broadening nor shift of Bragg angles was observed.

An alternative measure of the fraction decomposed, α_D, the relative decrease of peak heights of dolomite with time, was exmained. It may be called a "fractional destruction," being calculated from the intensity of the (104) lines of dolomite in heated samples. As is shown in Fig. 4, α_D was considerably larger than α' at any time. The reason may be one or more of the following. (a) Adsorption or occlusion of CO_2 on or in the small particles of amorphous MgO. (b) Formation of considerable amounts of point defects in the dolomite lattice, resulting in a large Debye–Waller factor. (c) Formation of so-called magnesian calcite. From the fact that calcite can contain $MgCO_3$ to ca. 10% at 700°C under CO_2 of the equilibrium pressure, as is shown in the phase diagram from Goldsmith and Heard (*11*), it seems likely that the last reason (c) is dominant.

Kinetics

(*a*) *Decomposition into $CaCO_3$ and MgO.* At temperatures lower than 812°C, the plots of $1 - (1 - \alpha')^{1/3}$ against t gave straight lines in the range of α' from 0 to 0.8. Thus the decomposition is an interfacial reaction and is expressed by the well-known equation

$$1 - (1 - \alpha')^{1/3} = kt. \tag{4}$$

The activation energy was calculated to be 69.5 kcal/mole, somewhat larger than that for $MgCO_3$, 65.4 kcal under a CO_2 of 17 cm Hg (*12*).

(*b*) *Decomposition into CaO and MgO.* Because the earlier stages of the reaction, in which $CaCO_3$ and MgO are formed, are too rapid to permit an accurate evaluation of the rate, only the latter processes, decomposition of the $CaCO_3$ into CaO, were examined at temperatures above 812°C. An alternative denotation, α'', may be used to express the fraction of the $CaCO_3$ decomposed, where $\alpha'' = (\alpha - 0.5)/(1\text{-}0.5)$. A linear relation between $1 - (1 - \alpha'')^{1/3}$ and t was observed again but in only a narrow range of α'', e.g., 0–0.3 at 860°C, 0–0.2 at 830°C. The character of these deviations from linearity is similar to that for the decomposition of small particles of calcite, which is strongly retarded by sintering during the calcination, especially under CO_2 (*13*). The activation energy for the linear range of the earlier stages was 220 kcal/mole. This abnormally high value is similar to that of calcite, 300 kcal for precipitated fine powder and 100–230 kcal for powdered single crystals, which was suggested to be a consequence of strong adsorption of CO_2 at the coherent interface between $CaCO_3$ and CaO (*13*).

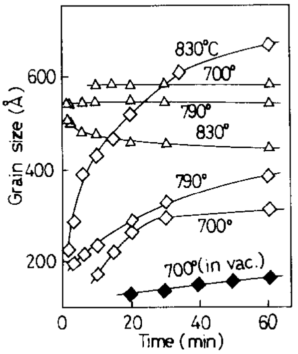

FIG. 5. Plots of grain sizes of products in decomposing dolomite against time. △, $CaCO_3$ (under CO_2 of 20 cm Hg); ◇, MgO (under CO_2 of 20 cm Hg); ◆, MgO (under vacuum, ca. 10^{-1} mm Hg).

Grain Sizes of Products

The grain sizes of $CaCO_3$ and MgO formed in the samples were determined from the Scherrer equation, using the half-maximum widths of the (104) and (220) reflections, respectively. $K\alpha$ doublet broadening was corrected using the curves given in Klug-Alexander's textbook (*14*), and a silicon standard was used to correct for instrumental broadening. Cauchy function was assumed for the lineshapes.

Although the obtained values have probably not been separated from the influence of lattice strain, which certainly is present in a decomposing phase, they were taken as a relative measure for the crystallizing behavior of the products.

The change of grain sizes with time at constant temperatures under a CO_2 pressure of 20 cm Hg is shown in Fig. 5. The crystallites of MgO grow with time and with temperature, as is usual for the solid products which are produced from calcined materials by nucleation and growth. On the other hand, the crystallites of $CaCO_3$ are relatively large even immediately after their formation and remain constant in size during the decomposition of dolomite, except in the runs at temperatures higher than 812°C where the decomposition of $CaCO_3$ causes a decrease of grain sizes with time.

In Fig. 6 are plotted the grain sizes of MgO and $CaCO_3$ in samples, which were heated at various temperatures for 90 min under CO_2 pressures of 20 or 60 cm Hg. The crystallites of MgO grow with temperature, but plateaus are observed in the temperature range where $CaCO_3$ is stable. The presence of $CaCO_3$ seems to hinder the growth of MgO beyond a limited size. At higher temperatures where $CaCO_3$ is unstable, the growth of MgO again becomes marked. A positive effect of the pressure of CO_2 on the grain sizes is also shown in this figure. This effect may be similar to that on the sintering of pure MgO, discussed previously elsewhere (e.g., (*15*)).

The formation of larger $CaCO_3$ crystallites at relatively lower temperatures (Fig. 5) seems unusual. However, some similar cases were reported in the literature, e.g., formation of Cr_2O_3 from chromium-ammonium-alum (*16*), and of ZnO from zinc hydroxycarbonate (*17*). At about 800°C, immediately below the decomposition temperature, $CaCO_3$ grows markedly. This may be explained on the basis of an enhanced diffusivity of the component ions.

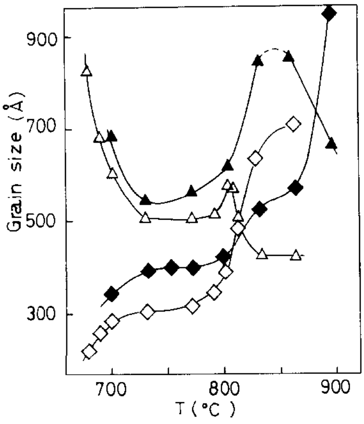

FIG. 6. Grain sizes of $CaCO_3$ and MgO formed in dolomite calcined for 90 min at various temperatures under CO_2. ▲, $CaCO_3$ (CO_2; 60 cm Hg); ◆, MgO (CO_2; 60 cm Hg); △, $CaCO_3$ (CO_2; 20 cm Hg); ◇, MgO (CO_2; 20 cm Hg).

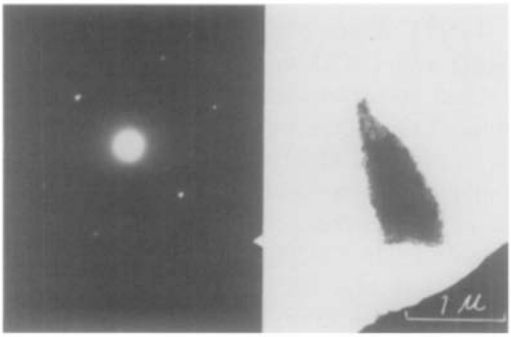

FIG. 7. Electron diffraction and microphotograph of calcined dolomite (830°C, 2 min, CO_2; 20 cm Hg).

Electron Diffraction

The electron diffraction pattern and photograph of the dolomite particle about 1 μm in size heated in CO_2 are given in Fig. 7.

The decomposed particles retain the forms of the parent dolomite; however, they are porous aggregates of a number of very fine particles.

For the sample heated at 830°C for 2 min under CO_2 pressure of 20 cm Hg, strong N spots are observed which apparently correspond to the reciprocal lattice of a calcite single crystal, and, in addition, a number of faint spots, from the remaining dolomite, are also recognized in the vicinities of the strong spots. This figure shows a very strong orientation of calcite crystallites in a coaxial state with the parent dolomite, in agreement with the results of Wilsdorf and Haul (*8*). Several short arcs, from MgO, are also observed in this figure. The crystallites of MgO seem to have a tendency to form with a preferred orientation. This observation is different from that of Wilsdorf and Haul. Several different orientations were assumed by the MgO, but dominant orientations placed the (100) or (110) planes of MgO parallel to the (104) planes of $CaCO_3$.

At 860°C under a higher pressure of CO_2, $CaCO_3$ was still somewhat orientated, but MgO was not.

Discussion

As mentioned in the introduction, there are two different classical theories for the mechanism of $CaCO_3$ formation when dolomite decomposes, i.e., direct formation expressed by Eq. (1) or (2), and recarbonization by Eq. (3a) or (3b).

Wilsdorf and Haul suggested that the former explanation is consistent with the strong orientation of $CaCO_3$ crystallites. The orientation of products suggests a topotactic decomposition which leads to a direct formation. But epitaxial growth can also produce orientated crystallites. Our kinetic observations show that the decomposition of dolomite is an interfacial reaction. Then, if CaO is a direct product, it would probably be in coherent contact with the surface of the parent dolomite. In this circumstance, an epitaxial recarbonization might well form the oriented products.

In spite of this possibility and of the argument for the recarbonization mechanism provided by Lange and Roesky, the direct formation theory is considered to be supported by the results of our study. The reasons are as follows.

(a) Even at high temperatures, where $CaCO_3$ is unstalble, $CaCO_3$, instead of CaO, is formed at the beginning of decomposition.

(b) Destruction of the dolomite lattice proceeds faster than the release of CO_2.

(c) Although MgO grows with time, particle sizes of $CaCO_3$ are constant during isothermal decomposition of dolomite. This is apparently similar to the results of Niepce *et al.* (*18*) in which it is shown that the particle size of the topotactic decomposition product is determined by the tolerance limit for the strains caused by the structural rearrangement and does not depend on the percentage decompostion.

(d) At lower temperatures larger crystallites of $CaCO_3$ are formed. If CaO and MgO are formed initially, their particles should be smaller at lower temperatures and the CaO should be converted to smaller particles of $CaCO_3$.

A classical theory, which is consistent with the direct formation of $CaCO_3$, is that which supposes that the first step of decomposition is the separation into two carbonates (Eq. (1)). For this initial step to occur Mg and Ca ions must migrate in the lattice to form respective domains of each carbonate. The free energy change of this reaction has been evaluated to be ca. 2 kcal/mole by Stout and Robie (*19*), that is, thermodynamically unfavorable in the range from 830 to 1136 K. Accordingly the tendency to dissociate cannot be considered the dominant driving force of the initiation.

On the other hand, it may be reasonable to suppose that CO_2 can easily be released at defects on the surface of dolomite, leaving O^{2-} ions. After release of CO_2 from such defects, Mg ions in the neighboring domains may move to the vicinities of O^{2-} ions with Ca ions migrating in the counter direction, tending to give a thermodynamically stable state. The role of diffusion in the reactant phase on decomposition has been emphasized by Searcy and Beruto (*20*).

A model for the decomposition process is depicted in Fig. 8. The migration or diffusion of ions occurs in the interfacial zone, and $CaCO_3$ is formed in this zone coherently to the surface of the dolomite lattice, mainly as a topotactic process. The lattice constants *a* of the $CaCO_3$ were in the range 4.93–4.97 Å, depending on the heating temperatures and time. These values may be smaller than that of natural calcite, 4.99 Å, because of the presence of Mg ions in a form of so-called magnesian calcite, and probably of Fe and Mn ions also.

MgO may be formed at first in an amorphous state and gradually crystallize, with a tendency to preferred orientation because of an influence of the original coordination of anions.

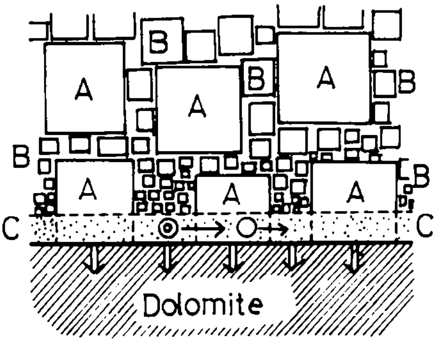

FIG. 8. Schematic model of decomposition of dolomite into $CaCO_3$ and MgO. A, $CaCO_3$; B, MgO (growth with time); C, interfacial zone; O, Mg ions; ◉, Ca ions.

At lower temperatures, the release of CO_2 and the crystallization of MgO proceed slowly, and then the diffusion of Ca and Mg ions in the interfacial zone can continue for a longer time and in wider domains, which favors formation of larger crystallites of $CaCO_3$.

Our analysis resembles the second theory expressed by Eq. (2), in which the evolution of CO_2 instead of the dissociation into two carbonates as in Eq. (1) initiates decomposition. But the product $CaCO_3 \cdot (1 - n)\ MgCO_3$ must be in the calcite phase instead of the dolomite phase.

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