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Agglomeration of magnesium oxide particles formed by the decomposition of magnesium hydroxide

Part 1 *Agglomeration at increasing temperature*

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Agglomeration of magnesium oxide (MgO) particles was studied by decomposing magnesium hydroxide ($Mg(OH)_2$). The properties of agglomerates varied according to the decomposition temperature region: (i) below 650° C, (ii) 650° C to 850° C, (iii) 850° C to 1050° C, and (iv) 1050° C to 1200° C. In region (i), the original $Mg(OH)_2$ frameworks or pseudomorphs remained in the powder and showed agglomeration. The strength of agglomerates containing the pesudomorphs was about 50 MPa; the primary particles in pseudomorphs are bonded chemically by the interaction of MgO and residual water. In region (ii) the pseudomorphs began to show some fragmentation: the bonding strength of these pseudomorphs reduced rapidly. In region (iii), both crystallite and primary particles were grown by the sintering; this growth may be due to an increase in contact area based on the collapse of pseudomorphs. The primary particles whose necks were grown by the sintering could be easily pulled apart by grinding. In region (iv) pore growth due to the rearrangement of primary particles caused the suppression of both densification rate and crystal growth of MgO.

1. Introduction

Magnesium oxide (MgO) powder is often obtained by the thermal decomposition of magnesium hydroxide ($Mg(OH)_2$). The resulting MgO powder contains hard or soft agglomerates.

Immediately after the decomposition of $Mg(OH)_2$ crystals, the minute MgO particles are observed to be held together strongly because they retain original frameworks or pseudomorphs [1–9]; these pseudomorphs deteriorate the compactivity since they offer resistance to the closer packing of particles [1]. Within the duration of the heating, however, the pseudomorphs are broken into fragments spontaneously by the propagation of cracks [1, 3, 5–9]. The properties of such agglomerates are also affected by the decomposition atmosphere [10]. Thus the agglomeration of MgO powder formed by the decomposition of $Mg(OH)_2$ is too complex for the whole process to be interpreted as a simple mechanism.

The agglomerate properties have previously been studied in the search for an easily sinterable powder, such as Al_2O_3 [11–14], Fe_2O_3 [15], Mullite [16], and ZrO_2 [17, 18]. A collapse of strongly bonded agglomerates through the grinding causes an improvement of sinterability of MgO powder [19, 20]. Numerous works were, therefore, directed towards the elimination of such agglomerates from a powder by grinding and sifting.

The present authors have already investigated the sinterability of MgO powders produced by various processes [21]. Since MgO powder is generally obtained by decomposing $Mg(OH)_2$ or basic magnesium carbonate, more information on the properties of the agglomerates, especially on those of the pseudomorphs, may help us to understand the overall sintering phenomenon.

This paper includes results for particle morphology, crystallite- and particle-growth behaviours, and bonding strengths of agglomerates formed by the decomposition of $Mg(OH)_2$.

2. Experimental details

2.1. Materials

The high purity commercially available $Mg(OH)_2$ (Iwatani Chemical Corp., 99.9% pure) was employed as a starting material; the $Mg(OH)_2$ powder was heated up to the desired temperatures in the region of 600° C to 1200° C at the rate of $10^\circ C\,min^{-1}$ in air and then was quenched to room temperature.

2.2. Thermal analyses

The decomposition process of $Mg(OH)_2$ was examined by differential thermal analysis (DTA) at the heating rate of $10^\circ C\,min^{-1}$ in air. The weight loss during heating was measured simultaneously by thermogravimetry (TG). The shrinkage of a $Mg(OH)_2$ disc (5 mm diameter and 3 mm high) pressed at 294 MPa was measured by using a dilatometer; the heating conditions were the same as those of the DTA-TG.

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2.3. Phase identification

The crystalline phases which occurred during the decomposition of $Mg(OH)_2$ were investigated by a high-temperature X-ray diffractometer (HT-XRD) with nickel-filtered $CuK\alpha_1$ radiation (Model Rad-IIA from Rigaku, Tokyo) at the heating rate of 10° C min^{-1} in air.

2.4. Measurement of crystallite size

The crystallite size (G_{XRD}) of MgO was obtained by the XRD technique in the following equation:

$$G_{XRD} = \frac{K\lambda}{\beta \cos \theta} \qquad (1)$$

where λ represents the wavelength of $CuK\alpha_1$, K is a shape factor ($=0.9$), β the half-height width of the (420) reflection, and θ the Bragg angle.

2.5. Measurements of specific surface area and pore-size distribution

Specific surface area (SSA) of the MgO powder obtained by the decomposition of $Mg(OH)_2$ was measured by BET technique, using nitrogen as an adsorption gas. Moreover, SSA of the powder ground for 10 min was measured by the same technique described above; the grinding machine with an agate mortar (Model AGA from Ishikawa Kojo MFG, Tokyo) was used in this experiment.

We assumed the particle to be cubic and calculated the primary-particle size (G_{BET}) from the following equation

$$G_{BET} = \frac{F}{\varrho S} \qquad (2)$$

where F represents a particle-shape factor ($F = 6$, assuming it to be cubic), ϱ the powder density and S the specific surface area.

The pore-size distribution of MgO powder was measured by mercury porosimetry.

2.6. Measurement of secondary-particle size distribution and observation of morphology

The secondary-particle size distribution of each powder was measured by centrifugal sedimentation, using ethyl alchohol as a dispersion medium. The average particle size, defined as G_{SED}, was determined by the arithmetic mean from the distribution curve. The morphology of the MgO particles was observed by transmission electron microscopy (TEM) (Model H-300 from Hitachi, Tokyo).

2.7. Measurement of relative density

The MgO powder was uniaxially pressed into a disc (5 mm in diameter and 3 mm in height); the steel die was lubricated on the die walls with stearic acid. The relative density (D_{Rela}) was obtained by the following equation

$$D_{Rela} = 100\frac{D_{Bulk}}{D_{Theo}} \qquad (3)$$

where D_{Theo} is the theoretical density and D_{Bulk} is the bulk density of the compact. Here the bulk density was calculated by measuring the weight and dimensions of the compressed body, whereas the theoretical density was calculated from the lattice parameter of MgO by XRD technique.

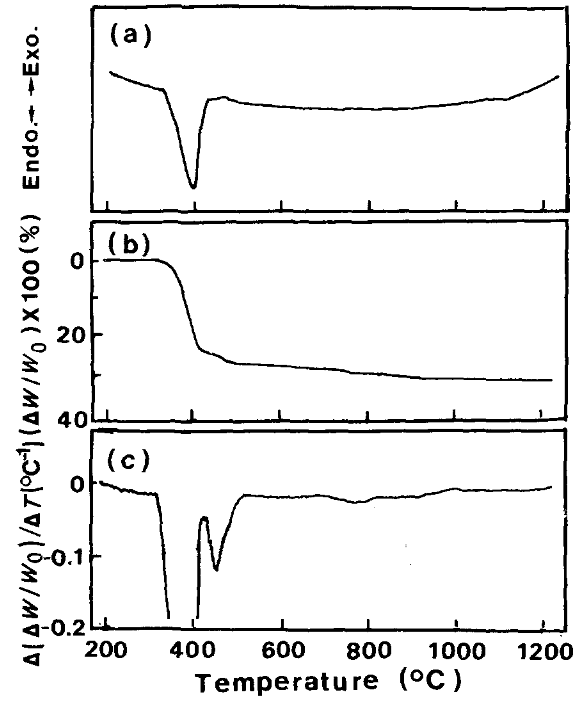

Figure 1 (a) DTA, (b) TG, and (c) DTG curves of $Mg(OH)_2$ heated at 10° C min^{-1} in air.

3. Results

3.1. Thermal analyses of $Mg(OH)_2$

The properties of MgO powder are strongly affected by the heating conditions of the precursor; thus the investigation of the decomposition process of the $Mg(OH)_2$ will give us fundamental information on the properties of MgO powder.

Fig. 1 shows the results of DTA, TG, and differential of TG (DTG). The DTA curve contained an endothermic effect at 320° C to 430° C. In this temperature range, 22.4% of the weight loss was found from the TG curve; after 3.0% of the step-wise weight loss occurred without a break up to 480° C, a slight amount of the weight loss continued on further heating up to around 1200° C. The results of TG were reflected in the DTG curve which contained two peaks in the range of 320° C to 480° C.

Fig. 2 shows the results of phase changes, examined

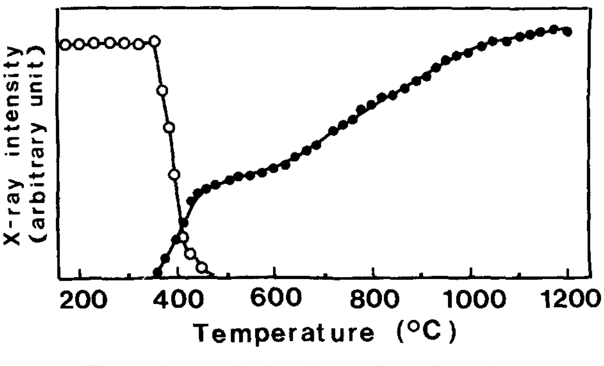

Figure 2 Phase changes during the heating of $Mg(OH)_2$ at the rate of 10° C min^{-1} in air (○ $Mg(OH)_2$ ($2\theta = 38.0°$), ● MgO ($2\theta = 42.9°$))

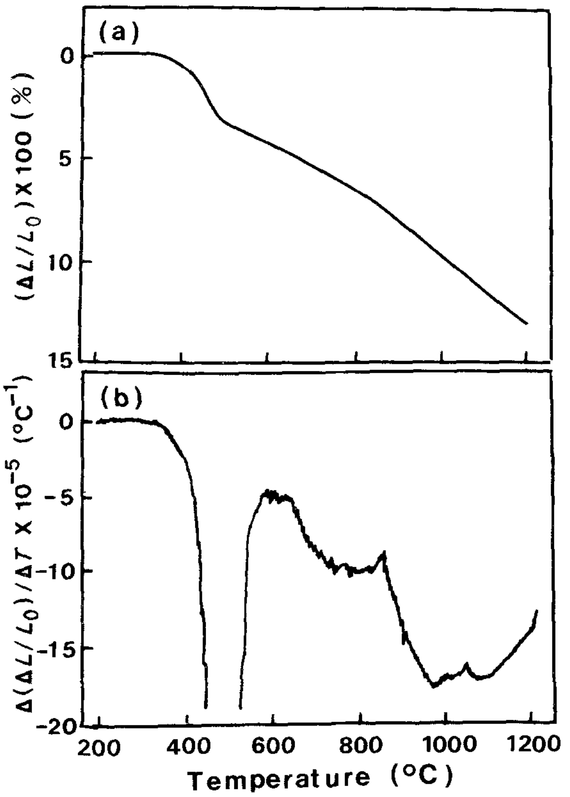

Figure 3 (a) Shrinkage and (b) differential shrinkage curves of $Mg(OH)_2$ compact heated at the rate of $10°C\,min^{-1}$ in air.

by HT-XRD. The original $Mg(OH)_2$ began to decompose at 340° C and, in turn, MgO appeared. Even after the $Mg(OH)_2$ disappeared at 500° C, MgO increased with increasing temperature up to 1200° C; however, this trend of an increase in MgO revealed two break points at 600° C and at 1050° C.

Fig. 3 shows a shrinkage and its differential curves of $Mg(OH)_2$ compact during heating; a contraction of the compact due to the decomposition of $Mg(OH)_2$ began to take place at about 350° C and proceeded on further heating up to 1200° C. The differential shrinkage curve contained four peaks, initiated at 350° C, 650° C, 850° C, and 1050° C.

3.2. Examinations of particle size and shape

It is found that a single phase of MgO forms at temperatures exceeding 500° C; consequently the properties of MgO powders were examined by decomposing the $Mg(OH)_2$ at and above 600° C.

Fig. 4 shows typical morphologies of MgO particles prepared by decomposing the $Mg(OH)_2$ at 600° C, 900° C, 1000° C, and 1200° C. At 600° C (Fig. 4a), minute particles (roughly 0.01 μm) were closely packed in about 0.3 μm of the original $Mg(OH)_2$ frameworks or the pseudomorphs. At 900° C (Fig. 4b), the external shape of these pseudomorphs became indistinct and, instead, many fragments were present in the powder; the particles were grown up to about 0.05 μm. At 1000° C (Fig. 4c), the pseudomorphs disappeared and, in turn, an agglomerate composed of roughly 0.05 μm of particles was present in the powder. At 1200° C (Fig. 4d), these particles, grown up to about 0.1 μm, adhered to each other to form agglomerates in which pores were about 0.2 μm in size.

Fig. 5 shows the changes of crystallite, primary-particle, and secondary-particle sizes as a function of

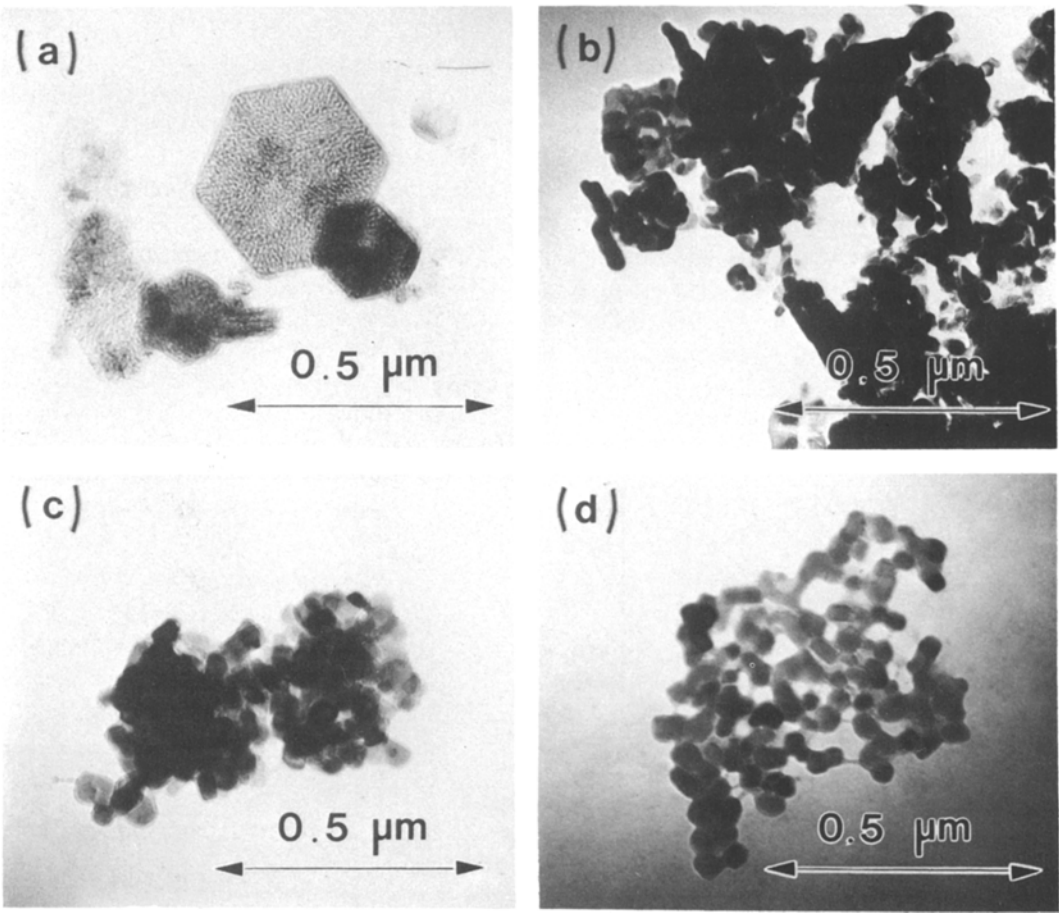

Figure 4 TEM photographs of MgO powders obtained by decomposing the $Mg(OH)_2$ at (a) 600° C, (b) 900° C, (c) 1000° C, and (d) 1200° C.

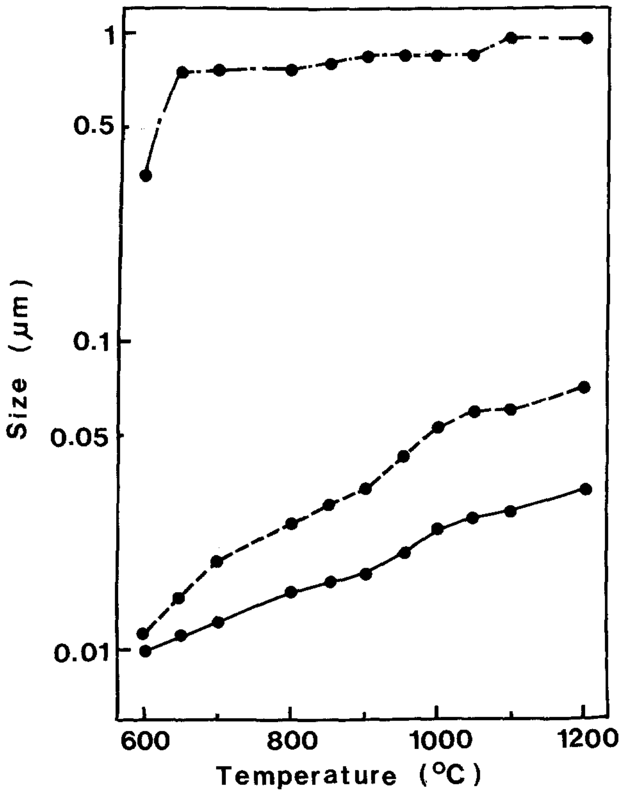

Figure 5 Changes in crystallite, primary-particle and secondary-particle sizes of MgO powder heated at the rate of $10°\mathrm{C\,min^{-1}}$ in air. (—— crystallite size, - - - primary-particle size, -·- secondary-particle size).

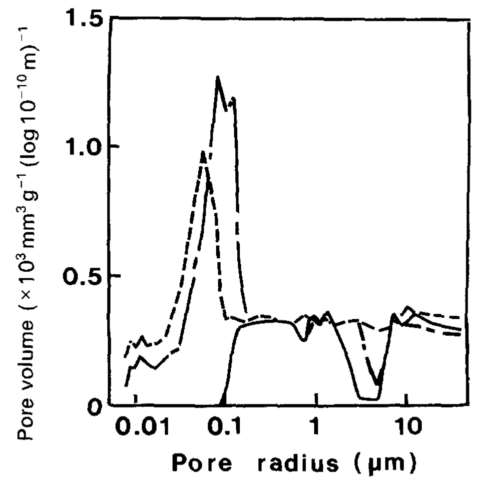

Figure 7 Typical pore-size distribution curves of MgO powders obtained by decomposing the $Mg(OH)_2$ at 600° C, 900° C, and 1200° C. (—— 600° C, - - - 900° C, -·- 1200° C).

temperature. The primary particle does not always consist of a single crystal but often of several crystallites. In addition, agglomerates composed of primary particles can be defined as a secondary particle. The MgO crystallite grew with increasing temperature; however, a sudden and stepwise growth was observed in the range of 900° C to 1000° C. The growth behaviour of primary particles was similar to that of crystallites; however, since the primary particle grew more rapidly than the crystallite, the primary particle size diverged from the crystallite size towards higher values with increasing temperature. The secondary particle grew rapidly in the range of 600° C to 650° C and then gradually with increasing temperature up to 1200° C.

The ratios of primary-particle size to crystallite size ($G_{\mathrm{BET}}/G_{\mathrm{XRD}}$) and of secondary-particle size to primary-particle size ($G_{\mathrm{SED}}/G_{\mathrm{BET}}$) are calculated on the basis of the above results; the cubes of these values are chosen to evaluate the degree of agglomeration of crystallites per primary particle (DA-CP) and that of primary particles per secondary particle (DA-PS). Results are shown in Fig. 6. The DA-CP enhanced in the range of 600° C to 1000° C and then reduced slightly on further heating up to 1200° C. The DA-PS enhanced suddenly in the range of 600° C to 650° C but reduced rapidly on further heating.

Fig. 7 shows the typical pore-size distributions of MgO powders obtained by decomposing the $Mg(OH)_2$ at 600° C, 900° C, and 1200° C. At 600° C, most of the pores were in the ranges of 0.08 μm to 3 μm and of 5 μm to 40 μm. At 900° C, a large amount of pore was present in the range of 0.01 μm to 0.1 μm. The pore-size distribution at 1200° C has shifted towards the values larger than those at 900° C.

3.3. Examination of agglomerate properties by grinding

The degree of agglomerate strength of MgO powder was evaluated by measuring the properties of ground powder.

Fig. 8 shows the relative changes in surface area of MgO powder ($\Delta S/S_0$; $\Delta S = S - S_0$) as a function

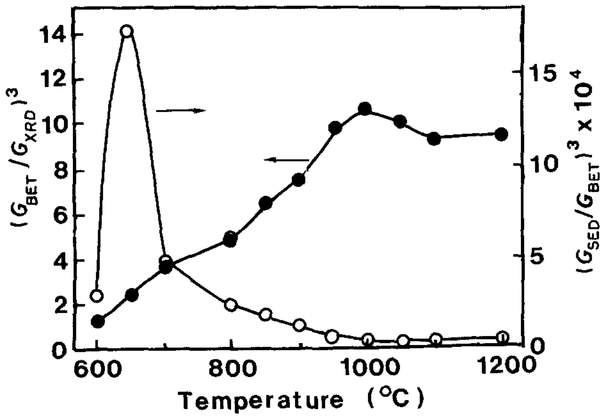

Figure 6 Changes in $(G_{\mathrm{BET}}/G_{\mathrm{XRD}})^3$ and $(G_{\mathrm{SED}}/G_{\mathrm{BET}})^3$ ratios of MgO powders heated at the rate of $10°\mathrm{C\,min^{-1}}$ in air.

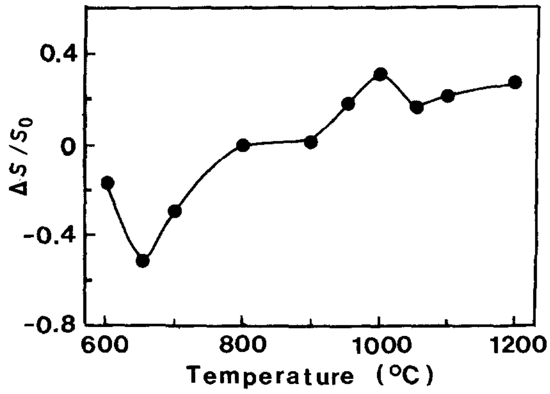

Figure 8 Changes in $\Delta S/S_0$ values by the grinding of MgO powders heated at the rate of $10°\mathrm{C\,min^{-1}}$ in air.

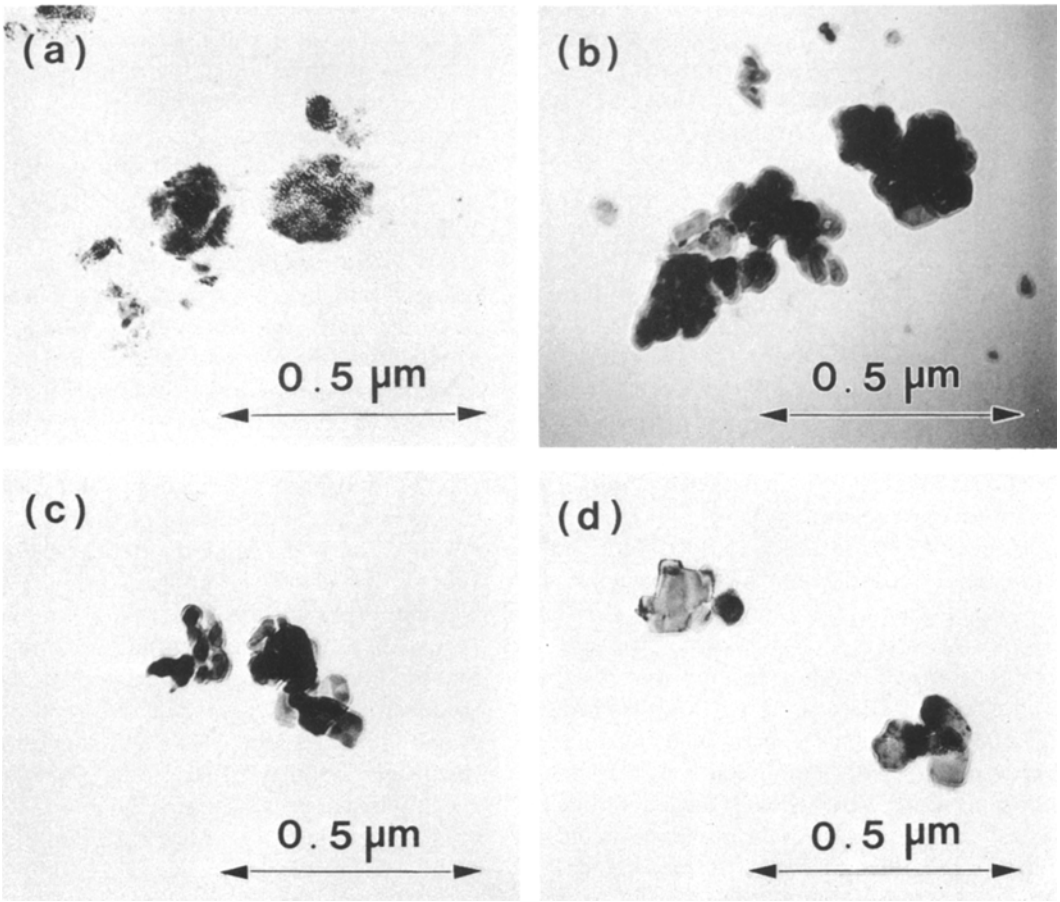

Figure 9 TEM photographs of ground MgO powders obtained by decomposing the $Mg(OH)_2$ at (a) 600° C, (b) 900° C, (c) 1000° C, and (d) 1200° C.

of temperature; here S_0 represents the SSA of as-decomposed powder and S that of the ground powder. The $\Delta S/S_0$ value reduced rapidly in the range of 600° C to 650° C and then increased up to 1000° C; it reduced slightly in the range of 1000° C to 1050° C and, on further heating, increased again.

Fig. 9 shows TEM photographs of the ground MgO powders. Even after the grinding (10 min) of MgO powder heated at 600° C (Fig. 9a), many pseudomorphs with their rounded edges still remained, together with their fragments. After the grinding of MgO powders heated at 900° C (Fig. 9b), 1000° C (Fig. 9c), and 1200° C (Fig. 9d), no pseudomorphs were observed but, in turn, agglomerates of the particles were present in the powder.

Fig. 10 shows the typical relationship between relative density and compressed pressure. The relative density of MgO powder heated at 600° C showed the break point at about 50 MPa; however, the MgO powders heated at 900° C and 1200° C were exponentially densified with increasing compressed pressure.

4. Discussion

4.1. Decomposition process of $Mg(OH)_2$ during heating

The differential shrinkage curve shows that the decomposition process of $Mg(OH)_2$ can be roughly divided into four regions: (i) 300° C to 650° C, (ii) 650° C to 850° C, (iii) 850° C to 1050° C, and (iv) 1050° C to 1200° C.

In region (i) the decomposition of $Mg(OH)_2$ brings about the formation of MgO. Although the temperature at which the $Mg(OH)_2$ compact initiates the contraction is somewhat higher than that of other results. The reason for this formation may be that the evolution of water vapour in the compact is being suppressed by a rise of its partial pressure. The decomposition of $Mg(OH)_2$ proceeds as follows

$$Mg(OH)_2 \rightarrow MgO + H_2O \qquad (4)$$

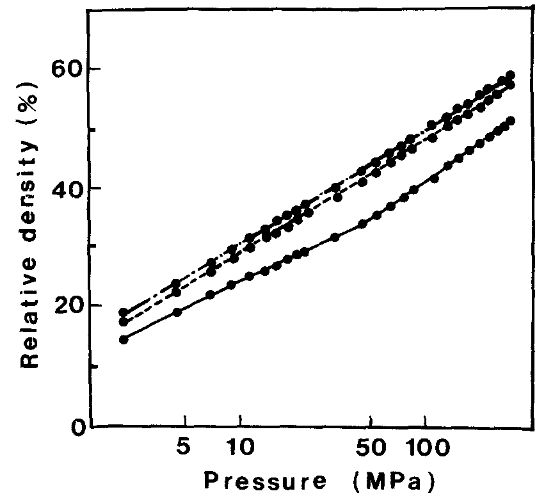

Figure 10 Typical relationship between relative density and compressed pressure of MgO powders obtained by decomposing the $Mg(OH)_2$ at 600° C, 900° C, and 1200° C. (—— 600° C, – – – 900° C, --- 1200° C).

Regardless of the single-stage reaction shown in Equation 4, the DTG curve contains another small peak; since the HT-XRD results show that a small amount of the $Mg(OH)_2$ vanishes in this region, the additional peak may be due to the decomposition of residual $Mg(OH)_2$.

In regions (ii), (iii) and (iv) the crystallinity of MgO progresses with increasing temperature; however, the trend of (ii) and (iii) is different from that of (iv). This fact indicates that the properties of MgO powder are altered at around 1050° C. The regions of (ii) and (iii) can only be distinguished by the results of the differential shrinkage curve, but not by those of the other data shown in Figs 1 and 2. The discussion of these differences in phenomena between regions (ii) and (iii) will be deferred until sufficient data will have been presented in the next section.

In the range of 650° C to 1200° C, most of the water has already been removed from the system, but a small amount of the residual water is still present. How the last traces of water remain in MgO powder was investigated by Livey *et al.* [1], who reported that residual water amounted to 0.12 wt % even at 1380° C. Longo *et al.* [22] analysed this phenomenon by using a three-dimensional model, and found that an interaction between MgO and water varied with the magnitude of the water vapour pressure. The proposed mechanisms for low and high water pressures are represented by Equation 5 and by Equation 6, respectively

$$Mg(MgO)_3 + H_2O \rightarrow (MgO)_3H + MgOH + V \tag{5}$$

$$Mg(MgO)_3 + nH_2O \rightarrow (MgO)_3 \cdot 2H + Mg(OH)_2(n-2)H_2O + V \tag{6}$$

where V is a magnesium vacancy, n is an integral number (2 or 3), and $Mg(MgO)_3$ indicates a corner of magnesium atom bonded by three mutually perpendicular MgO molecules. When the residual water decreases with increasing temperature, the mechanism of an interaction between MgO and water will be altered from Equation 6 into Equation 5. The effect of water vapour on properties of MgO particles will be discussed in the next section.

4.2. Changes in properties of MgO powder during heating

The discussion will be simplified by dividing the phenomena into four temperature regions, as mentioned above.

4.2.1. Below 650° C

The properties of MgO powder heated at 600° C are worthy of notice. The value of DA-CP is nearly unity, which indicates that most of the primary-particles are composed of single crystals in this region. These results have also been confirmed by many investigators through a study of the selected area diffraction patterns [3, 4, 8, 9]. The particle size in the pseudomorphs observed by TEM is roughly in accord with the primary-particle size. The average size of pseudomorphs, estimated to be 0.3 μm by TEM observation, agrees with the secondary-particle size. The pores between pseudomorphs are chiefly in the range of 0.08 μm to 3 μm, while those between clusters of the pseudomorphs are in the range of 5 μm to 40 μm; some pores below the limit size of detection, i.e. 0.0735 μm, by mercury porosimetry, are also probable in pseudomorphs as minute cracks or as cleavages formed during the decomposition of $Mg(OH)_2$ [8, 9]. When MgO powder is compressed due to changing pressure, the rearrangement of agglomerates, chiefly of pseudomorphs, may proceed at the lower pressure; after the hard agglomerates or pseudomorphs are broken into fragments at around 50 MPa, these fragments rearrange to form a closer packing at the higher pressure. The presence of pseudomorphs may thus deteriorate the compaction of MgO powder. Similar results have been obtained by Hamano [23], who observed a decrease in compactivity of MgO powder when he heated the $Mg(OH)_2$ in the range of 500° C to 700° C. The strong bonding of primary particles in pseudomorphs can be explained as an interaction of MgO with water. Sakamoto and Yamamoto [24] found that the strength of a glass pellet bonded chemically by the reaction of water was one thousand times as high as that of a dried pellet. They estimated the strength of chemically bonded pellet to be 64 MPa, which is roughly in accord with the value of 50 MPa obtained in this experiment; it is noteworthy that the strength of such a chemically bonded pellet exhibits the same magnitude as that of a sintered pellet. The strong bonding between particles can also be verified by the fact that many pseudomorphs still retain their original frameworks even after grinding.

The DA-PS increases rapidly with increasing temperature and shows a maximum at 650° C. This behaviour can be explained by the agglomerations not only of primary particles but also of pseudomorphs. Such agglomerations will result in a reduction of surface area by the adhesion of fine particles, which will lower the excess energy [25]; the residual water may also contribute to the agglomeration of MgO particles by the active surface diffusion, through the reactions of Equations 5 and 6. The grinding of MgO powder makes the $\Delta S/S_0$ value negative in this temperature region, which indicates that the fragmentation of pseudomorphs is less dominant than the reagglomeration of broken fragments; an increase in contact area based on the compression force by the grinding may accelerate the adhesion of MgO particles due to the electrical attraction force [26–28], van der Waals force [26], the capillary force of water adsorped on the surface [26].

4.2.2. In the region of 650° C to 850° C

A rapid decrease in DA-PS with increasing temperature suggests not only the growth of primary particles but also the fragmentation of pseudomorphs; the fragmentation may be carried out by the reduction of chemical bonding between particles due to a decrease in the amount of residual water and by the creation of cracks based on the stress [3, 9] formed during the decomposition of $Mg(OH)_2$. A contraction of $Mg(OH)_2$ compact in this temperature region also suggests the fragmentation of pseudomorphs.

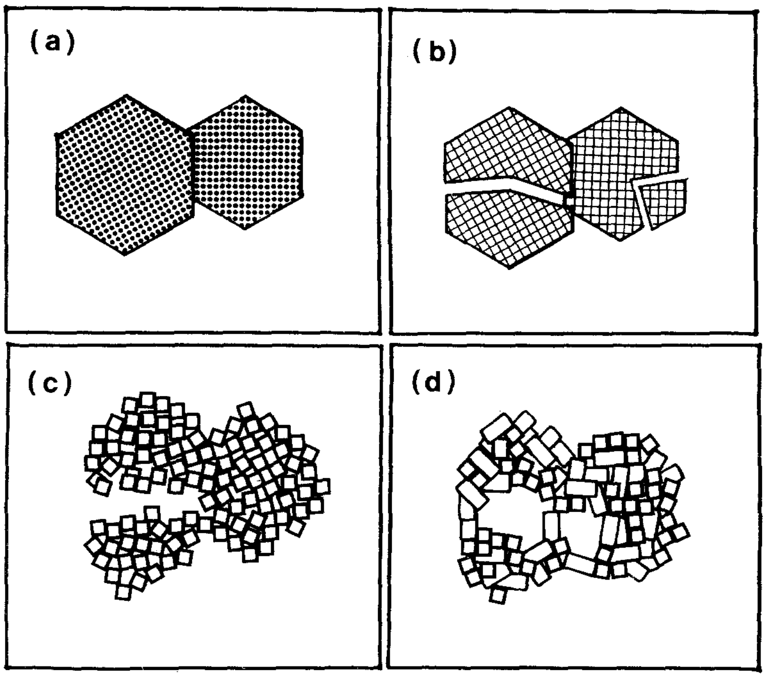

Figure 11 Model for agglomeration process of MgO powder obtained by decomposing the $Mg(OH)_2$. (a) Below 650° C, (b) in the region of 650° C to 850° C (c) in the region of 850° C to 1050° C, and (d) in the region of 1050° C to 1200° C.

The $\Delta S/S_0$ value which is negative at 650° C recovers to zero at 800° C; thus the grinding of MgO powder reaches a physical equilibrium between fragmentation and reagglomeration [27]. The enhanced contribution of fragmentation to the powder by grinding may be attributed to the reduction of surface activity by both crystallite and primary-particle growth.

4.2.3. In the region of 850° C to 1050° C

The enhanced growth of crystallite and primary particle in this temperature region can be related to a rapid contraction which occurs during the heating of $Mg(OH)_2$ compact. These phenomena are ascribed to a sintering among particles. The mass transfer is activated chiefly by an increase in contact area between crystallites and between primary particles due to their rearrangement. It may also be accelerated by an increase in the magnesium vacancies formed by the interaction of MgO with the last traces of residual water. Most of the pores are in the range of 0.01 μm to 0.1 μm; it is inferred that these pores are formed by the rearrangement of primary particles during the sintering. The rapid progress in coalescence of primary particles could be confirmed by the observation of a temporary suppression of the weight loss in the TG curve. The rearrangement of particles during the initial stage of sintering has been pointed out by many investigators [29, 30] from the measurements of isothermal shrinkage curve, pore-size distribution, and surface area.

After DA-CP increases with increasing temperature up to 1000° C, it decreases slightly. On the other hand, DA-PS stops reducing above 1000° C. These phenomena indicate that the physical properties change at around 1000° C; details will be discussed later.

The grinding of the powder leads to a rapid increase in $\Delta S/S_0$ value in the range of 900° C to 1000° C. This fact suggests that the particles whose necks are grown by the sintering may be easily pulled apart in the initial stage of sintering. Nevertheless, a slight decrease in $\Delta S/S_0$ value takes place in the range of 1000° C to 1050° C, which suggests the enhancement of bonding strength between primary particles.

The fact that no break point appears in the density–pressure curve of MgO powder heated at 900° C suggests the disappearance of the hard agglomerate, i.e. the collapse of pseudomorphs and the weakness for bonding strength of primary particles; it is confirmed from these results that the bonding strength of primary particles in pseudomorphs is much stronger than that of primary particles in the initial stage of sintering.

4.2.4. In the region of 1050° C to 1200° C

The value of DA-CP reduced slightly, suppressing the crystallinity and densification of MgO. A comparison of the pore-size distribution at 1200° C with that at 900° C reveals that pores between primary particles grow with increasing temperature; the pore growth could also be confirmed by the TEM observation. It is thought that the pore growth proceeds rapidly due to their coalescence and the rearrangement of particles; such a pore migration may lead to a suppression of the densification. The behaviour of pore growth during the initial stage of sintering has already been reported by Whittemore and Sipe [31]; as the fine particles densify, large pores develop through the interstices of the large particles, resulting in an increase in pore size with little change in total porosity or in densification.

The gradual increase in $\Delta S/S_0$ value in this region indicates the slight reduction of bonding strength, which is brought about by the coalescence of pores.

As already mentioned in Sections 4.2.1 to 4.2.4, the agglomeration process of MgO powder derived from the $Mg(OH)_2$ could be divided into four stages. Fig. 11 shows their schematic diagrams. Below 650° C (Fig. 11a), the original $Mg(OH)_2$ frameworks or pseudomorphs remain; their agglomeration proceeds rapidly. In the region of 650° C to 850° C (Fig. 11b), these pseudomorphs begin to show some fragmentation. In the region of 850° C to 1050° C

(Fig. 11c), crystallites and primary particles begin to show the sintering. Above 1050° C (Fig. 11d), the rearrangement of primary particles leads to the pore migration, resulting in the pore growth.

5. Conclusion

The agglomeration process of MgO particles formed by the decomposition of $Mg(OH)_2$ was studied from room temperature up to 1200° C. The agglomerate properties varied according to the decomposition temperature range: (i) below 650° C, (ii) 650° C to 850° C, (iii) 850° C to 1050° C, (iv) 1050° C to 1200° C. The results obtained were as follows.

(1) In the region below 650° C, many original $Mg(OH)_2$ frameworks or pseudomorphs remained; their agglomeration proceeded rapidly. The strength of agglomerates containing the pseudomorphs, evaluated to be about 50 MPa, may be a result of the chemical bonding interaction of MgO and residual water.

(2) In the region of 650° C to 850° C, the pseudomorphs began to show some fragmentation; the bonding strength of these pseudomorphs reduced rapidly.

(3) In the region of 850° C to 1050° C, the pseudomorphs disappeared and individual particles began to show the sintering; the primary particles whose necks were grown by the sintering could be easily pulled apart by the grinding.

(4) In the region of 1050° C to 1200° C, the pore growth due to the rearrangement of primary particles caused a suppression of both densification rate and crystal growth of MgO.

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