

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

Part 2 Agglomeration at fixed temperatures

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The agglomeration process of MgO powder derived from Mg(OH)₂ was investigated at fixed temperatures of 600, 800, 900 and 1200°C; these temperatures were chosen as representative of four regions, i.e. below 600°C, 650 to 850°C, 850 to 1050°C and 1050 to 1200°C previously reported. At 600°C, coherent crystallites coalesced within the heating time of 60 min; on further heating till 300 min, the primary particles which consisted of crystallites grew rapidly. The original Mg(OH)₂ framework or pseudomorphs, composed of minute crystallites and primary particles, still remained in the powder. At 800°C, the pseudomorphs had disintegrated into fragments. The crystallite growth and primary particle growth were accelerated with increasing the heating times beyond 60 min. At 900°C, a further fragmentation of agglomerates occurred with increasing the heating times; the crystallite and primary particle growth in fragments brought about the pore coalescence. At 1200°C, the crystallite and primary particle growth proceeded with the coarsening of pores; on heating beyond 240 min, the crystallites and primary particles grew rapidly due to the entrapment of pores within them.

1. Introduction

Magnesium oxide (MgO) powder is often produced by the thermal decomposition of magnesium hydroxide (Mg(OH)₂). The properties of the resulting MgO powder are strongly affected by the temperature and time taken for decomposing the Mg(OH)₂. Thus a great deal of investigation on the decomposition conditions has been carried out to establish the properties of MgO powder [1-5].

Recently, many researchers have devoted considerable attention to the properties of agglomerates in the powders of Al₂O₃ [6-9], Fe₂O₃ [10], mullite [11] and ZrO₂ [12, 13], on the grounds that a preferential intra-agglomerate sintering over inter-agglomerate sintering may bring about an inhomogeneous texture. The authors have also investigated the agglomerate process of MgO powder derived from Mg(OH)₂ at increasing temperatures; we found that the agglomerate properties varied from one of the following temperature regions to the next: below 650°C, 650 to 850°C, 850 to 1050°C and 1050 to 1200°C [14].

In this paper, we chose four temperatures: 600, 800, 900 and 1200°C, one for each temperature region and investigated (1) particle morphology, (2) crystallite and particle growth behaviours and (3) properties of agglomerates during the fixed heating.

2. Experimental details

2.1. Materials

High purity commercially available Mg(OH)₂ (Iwatani

Chemical Corp., 99.9% pure) was employed as a starting material. The original Mg(OH)₂ powder was heated up to the desired temperature at the rate of 10°C min⁻¹ and was then kept at this temperature for various times in the range of 10 to 300 min.

2.2. Measurements of X-ray peak intensity and crystallite size of MgO

The original Mg(OH)₂ powder was spread in a thin layer on a platinum foil and was then heated up to the desired temperature at the rate of 10°C min⁻¹. The profile of the (200) reflection of MgO was recorded continuously by using a high-temperature X-ray diffractometer (HT-XRD) with Ni-filtered CuKα₁ (Model RAD-IIA from Rigaku, Tokyo) at each fixed temperature. The crystallite size on the basis of the (420) reflection of MgO was obtained by Scherrer's formula.

2.3. Measurement of specific surface area (SSA) and calculation of primary particle size

SSA of the MgO powder obtained by the decomposition of Mg(OH)₂ was measured by a BET technique, using N₂ gas as an adsorption gas. Moreover, SSA of the powder ground for 10 min was measured by the technique described above; the grinding machine with an agate mortar (Model AGA Ishikawa Kojo MFG, Tokyo) was used in this experiment.

The primary particle size (G_{BET}) was obtained by assuming the particle to be cubic.

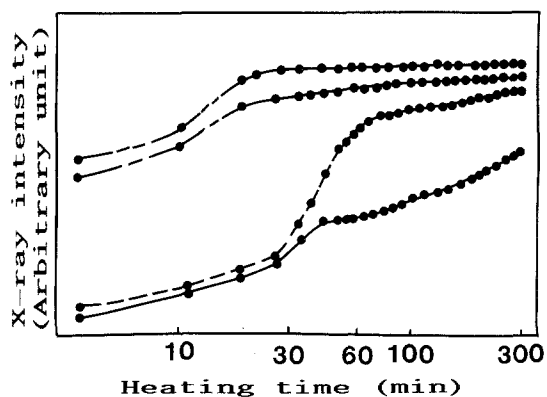


Figure 1 Changes in X-ray peak intensity of MgO ($2\theta = 42.9^\circ$) during heating at a fixed temperature in air. (●—●) 600°C; (●---●) 800°C; (●- - -●) 900°C; (●- - - -●) 1200°C.

2.4. Measurement of secondary particle size distribution and observation of morphology

The secondary particle size of each powder was measured by centrifugal sedimentation technique, using ethyl alcohol as a dispersion medium. The morphology of the MgO particles was observed by

transmission electron microscopy (TEM) (Model H-300 from Hitachi, Tokyo).

2.5. Measurement of tap density

About 1 g of the powder was poured in a cylinder (7.5 mm in diameter). Tapping was then performed at the rate of 60 taps min^{-1} ; the height for tapping was 25 mm.

2.6. Measurement of relative density

The MgO powder was uniaxially pressed into a disk (5 mm in diameter and 3 mm in height); the steel die was lubricated on the die walls with stearic acid. The relative density of the compact was obtained by dividing the bulk density by the theoretical density of the compacts. 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 techniques.

3. Results

3.1. Changes in crystallinity of MgO

Figure 1 shows the changes in X-ray peak intensity of

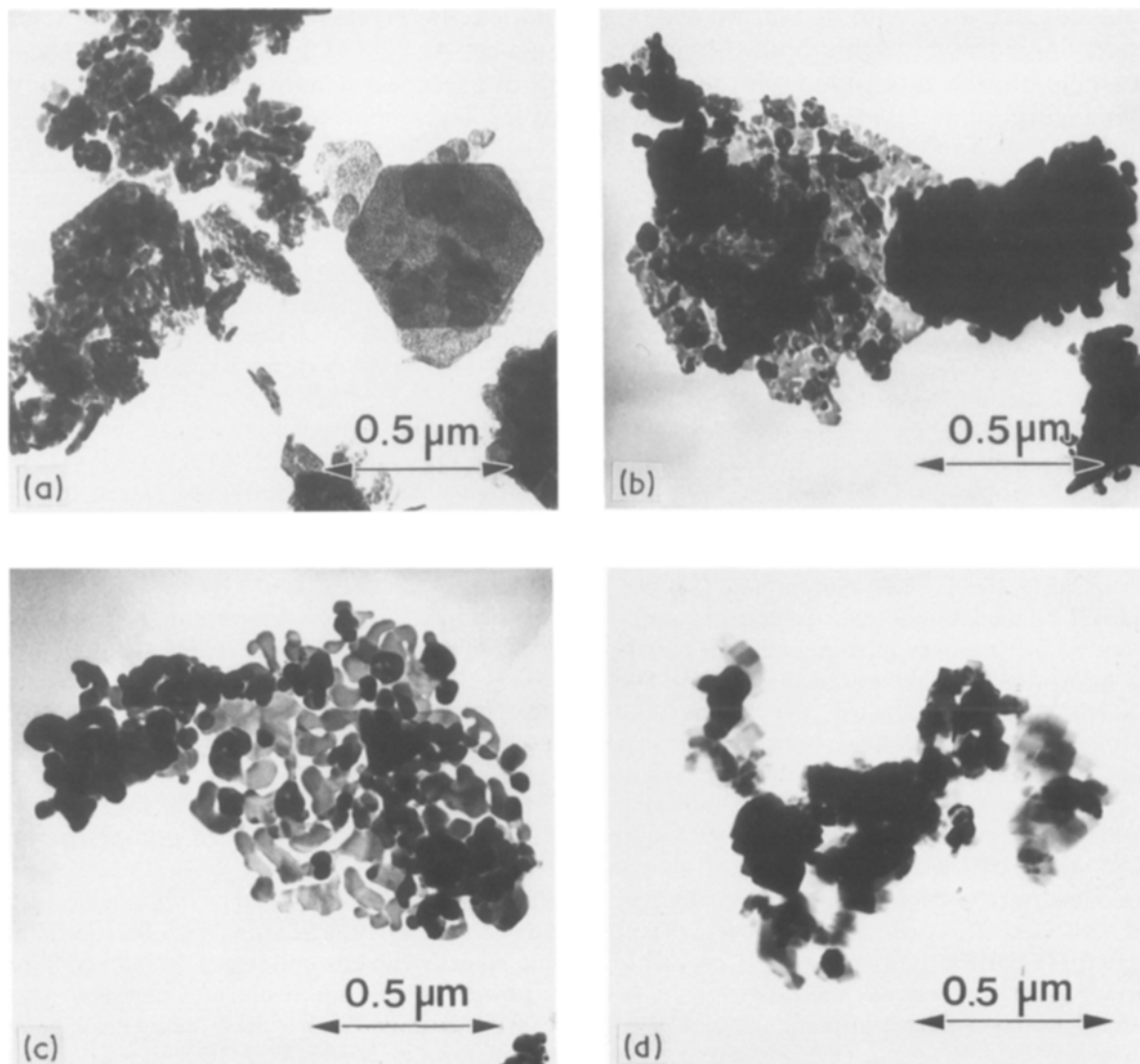


Figure 2 TEM photographs of MgO powders obtained by decomposing the $\text{Mg}(\text{OH})_2$ at (a) 600°C, (b) 800°C, (c) 900°C and (d) 1200°C for 300 min.

MgO at the fixed temperatures of 600, 800, 900 and 1200°C. At each temperature, the peak intensity increased with increasing times; these curves, which described S shapes, could be divided into two types: the type (1) curves at 600 and 800°C and the type (2) curves at 900 and 1200°C. In the type (1) curves, at 600 and 800°C, a sudden and stepwise increase in peak intensity of MgO was observed in the range of 25 to 100 min; on further heating, however, the peak intensity of MgO at 800°C diverged from that at 600°C, towards higher values. In the type (2) curves, 900 and 1200°C, the X-ray peak intensity of MgO hardly increased till 300 min after it had enhanced rapidly within the first 30 min.

3.2. Morphology of MgO particles

Figure 2 shows the morphologies of MgO particles heated at 600, 800, 900 or 1200°C for 300 min. The photograph of the MgO powder heated at 600°C for 300 min (Fig. 2a) shows that the minute particles (roughly 0.05 μm) are closely packed in about 0.5 μm of original Mg(OH)₂ frameworks or pseudomorphs. That of the MgO powder heated at 800°C for 300 min (Fig. 2b) shows that these hexagonal pseudomorphs and their fragments are held together to form agglomerates. That of the MgO powder heated at 900°C for 300 min (Fig. 2c) shows that the MgO particles, which appear to be vermicular-shaped, bond with each other; large pores are present between particles. That of the MgO powder heated at 1200°C for 300 min (Fig. 2d) shows that the cubic particles have coagulated to form an agglomerate.

3.3. Crystallite, primary particle and secondary particle sizes

3.3.1. Crystallite size

Figure 3 shows the effect of heating time on MgO crystallite growth at 600, 800, 900 and 1200°C. The overall trend is that the crystallite growth proceeded with increasing the heating times. As the arrow marks indicate, the crystallite growth was accelerated slightly beyond 60 min at 600, 800 and 900°C; at 1200°C,

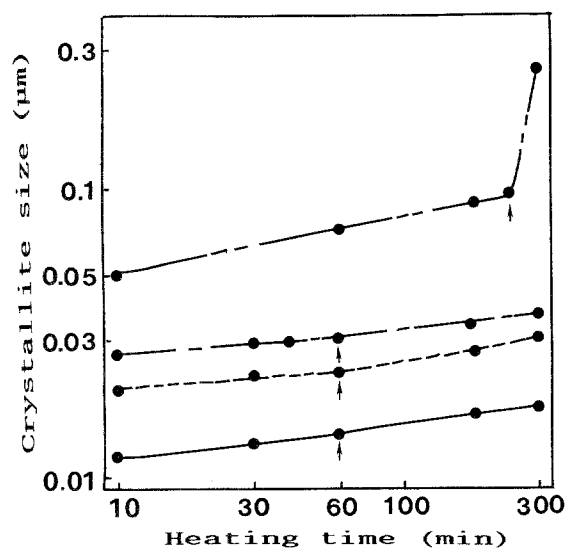


Figure 3 Changes in crystallite size of MgO during heating at fixed temperature in air; arrow marks indicate the break points. (●—●) 600°C; (●---●) 800°C; (●····●) 900°C; (●-·-·●) 1200°C.

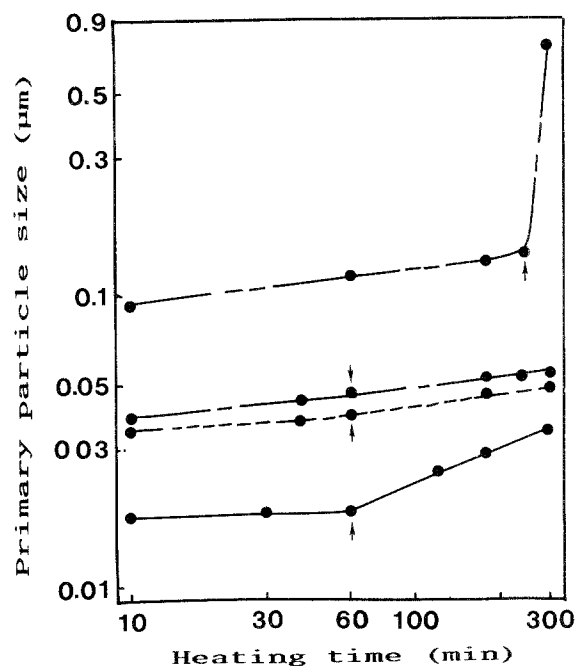


Figure 4 Changes in primary particle size of MgO during heating at fixed temperature in air; arrow marks indicate the break points. (●—●) 600°C; (●---●) 800°C; (●····●) 900°C; (●-·-·●) 1200°C.

however, a rapid crystallite growth occurred on heating beyond 240 min.

3.3.2. Primary particle size

Figure 4 shows the effect of heating time on primary particle growth at 600, 800, 900 and 1200°C. The primary particle does not always consist of a single crystal but often of several crystallites. The primary particles grew with increasing the heating times; as the arrow marks indicate, the primary particle growth was accelerated beyond 60 min at 600, 800 and 900°C; at 1200°C, however, a rapid primary particle growth was observed beyond the heating time 240 min.

3.3.3. Degree of agglomeration of crystallites per primary particle (DA-CP)

Figure 5 shows the changes in $(G_{\text{BET}}/G_{\text{XRD}})^3$ value, defined as a DA-CP, during heatings at 600, 800, 900 and 1200°C; the higher the DA-CP value is, the more the agglomeration of crystallites has proceeded. At 600°C, the DA-CP value decreased from four to two with increasing the heating times from 10 to 60 min; on heating till 300 min, however, it increased up to eight. At 800 and 900°C, the gradual decrease in DA-CP value resulted in a minimum at heating time of 60 min; on heating till 300 min, however, it increased again slightly and reached around five. At 1200°C, the DA-CP value decreased from seven to four within the heating time of 240 min; on heating, however, it increased rapidly and became 23 after heating for 300 min.

3.3.4. Secondary particle size

Figure 6 shows the distribution curves of secondary particle sizes in MgO powders heated at 600, 800, 900 and 1200°C. Here the agglomerates composed of primary particles can be defined as a secondary particle.

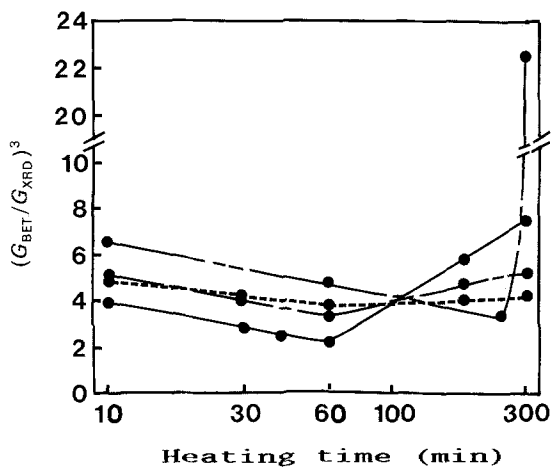


Figure 5 Changes in $(G_{\text{BET}}/G_{\text{XRD}})^3$ ratio of MgO powder during heating at a fixed temperature in air. (●—●) 600°C; (●---●) 800°C; (●····●) 900°C; (●- - -●) 1200°C.

At 600°C, the secondary particle size did not change regardless of any increase in heating time. Similarly, no marked change in secondary particle size was observed in MgO powders heated at 800°C for 10 min and for 60 min; however, the secondary particles in powder heated for 300 min showed an agglomeration, resulting in an increase in particles of average size 1.4 μm . At 900°C, the secondary particle size decreased slightly with increasing the heating times from 10 to 300 min. At 1200°C, the particles with average size 0.2 μm increased from 35 up to 45% as the heating time was prolonged from 10 to 60 min; however, the heating of MgO powder till 300 min increased the particles with an average size of 1.0 μm .

3.4. Agglomerate properties

3.4.1. Densification process by tapping

Figure 7 shows tap densities of MgO powder heated at 600, 800, 900 and 1200°C. These MgO powders densified gradually with an increase in tapping

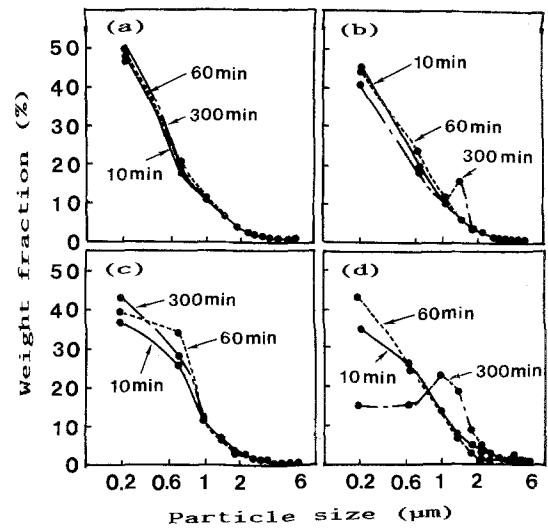


Figure 6 Secondary particle size distributions of MgO powders heated at (a) 600°C, (b) 800°C, (c) 900°C and (d) 1200°C in air; times indicate the heating periods.

number; however, the tap density varied according to the heating temperature and time of the MgO powder.

Among the MgO powders heated at 600°C, a rapid increase in tap density was observed when the heating time was prolonged from 60 to 300 min; at 800°C, such a rapid increase in tap density was achieved within 60 min. The tap densities of MgO powders heated at 900°C were much alike, independent of the heating time. The tap density of MgO powder heated at 1200°C was enhanced as the heating time was prolonged from 60 to 300 min; the MgO powder heated for 300 min showed that a stepwise increase in density was observed at around 500 taps.

3.4.2. Agglomerate strength

Figure 8 shows the relationship between relative density and compressive pressure of the MgO powder; samples for examining the agglomerate strength were

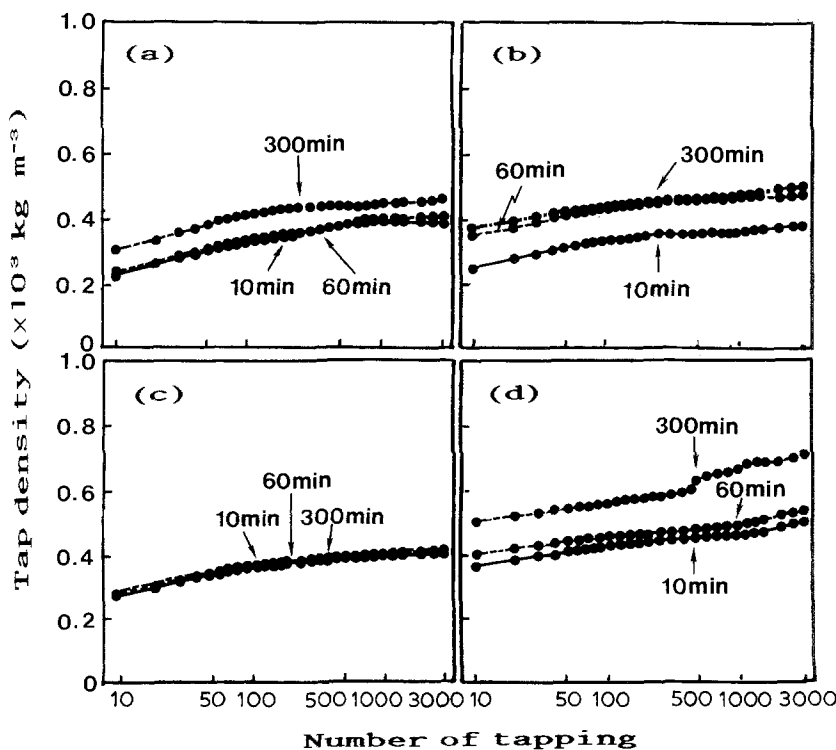


Figure 7 Relationship between tap density and number of tapping of MgO powder obtained by decomposing the $\text{Mg}(\text{OH})_2$ at (a) 600°C, (b) 800°C, (c) 900°C and (d) 1200°C; times indicate the heating periods.

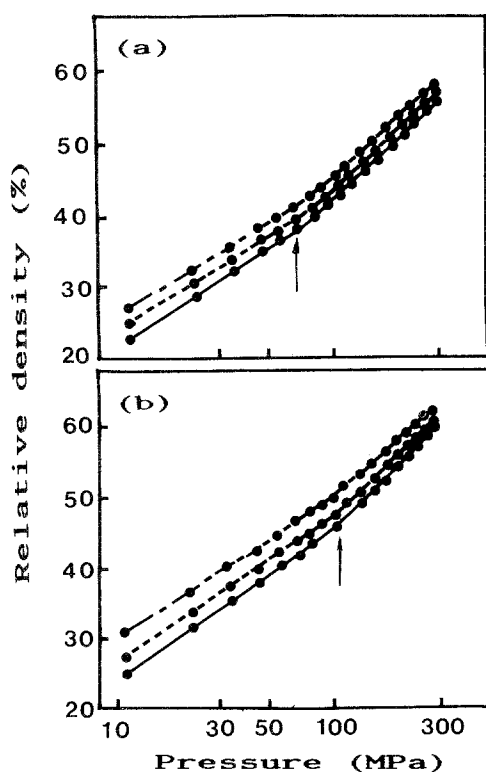


Figure 8 Relationship between relative density and compressive pressure of MgO powder obtained by decomposing the $\text{Mg}(\text{OH})_2$ at (a) 600°C and (b) 800°C for (—) 10 min, (---) 60 min and (---) 300 min; arrow marks indicate the break points.

restricted to the powders heated at 600°C and 800°C , since hard agglomerates were present in powders heated at temperatures less than 900°C [14]. As the arrow marks indicate, the relationship between relative density and compressive pressure of the powder heated at 600°C could be expressed as two straight lines intersecting at around 70 MPa (Fig. 8a); such a position, where the break point appeared, was not changed with increasing the heating times. The break point shifted to around 100 MPa in the powder heated at 800°C (Fig. 8b).

Figure 9 shows the relationship between SSAs before and after grinding the MgO powders heated at 900°C and 1200°C . Here the subtraction of solid from dotted lines indicates an increase in magnitude of SSA by grinding. The relation could be expressed as two stages intersecting at around $15\text{ m}^2\text{ g}^{-1}$ SSA of as-prepared powder, independent of the heating time and temperature. At $15\text{ m}^2\text{ g}^{-1}$ or higher SSA, the SSA is increased by about 10% by grinding the as-prepared powder; at $15\text{ m}^2\text{ g}^{-1}$ or lower SSA, the SSA was recovered markedly by grinding the MgO powder.

4. Discussion

4.1. Agglomeration process at 600°C

The $DA-CP$ value, defined as the degree of agglomeration of crystallites within a primary particle, was almost unity when the temperature reached 600°C [14]; this proves that the crystallites are composed of single crystals at this stage. When the MgO powder is heated at 600°C for 10 min, these crystallites are agglomerated spontaneously and the $DA-CP$ value rises to four; agglomeration occurs to lower the anisotropic surface energy and is accelerated by the

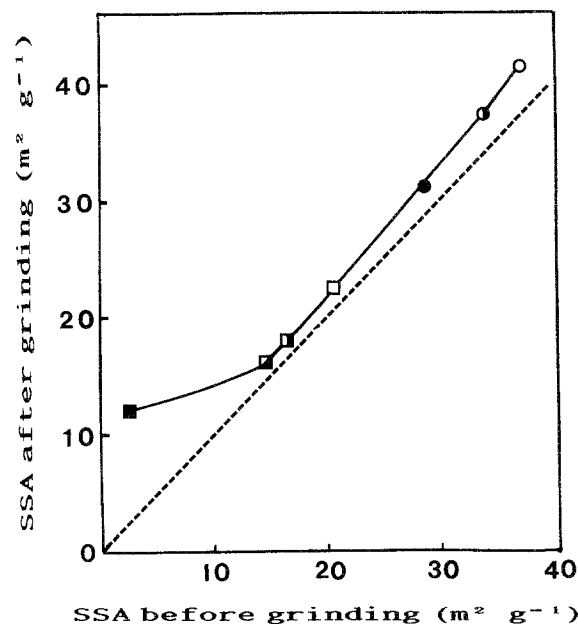


Figure 9 Relationship between specific surface areas (SSA) before and after grinding the MgO powders. Heating conditions: (○) 900°C , 10 min; (●) 900°C , 60 min; (●) 900°C , 300 min; (□) 1200°C , 10 min; (□) 1200°C , 60 min; (■) 1200°C , 240 min; (■) 1200°C , 300 min.

initial arrangement of MgO crystals with parallel $\{100\}$ faces [15, 16]. The coherent crystallites are then coalesced within a primary particle, which may bring about the reduction of $DA-CP$ value from four to two during heating from 10 to 60 min. It seems that the coalescence of MgO crystallites contributes to enhancing the crystallinity of MgO, which may be achieved by reducing the number of lattice defects [17].

With an increase in the heating times from 60 to 300 min, the crystallite growth is accelerated slightly. Kotera *et al.* [2] confirmed this phenomenon and explained it as the surface adhesion of crystallites. The $DA-CP$ value rises to about eight, so that an agglomeration of primary particle growth may predominate over that due to crystallite growth at this stage.

The MgO powder heated at 600°C contains original $\text{Mg}(\text{OH})_2$ frameworks or pseudomorphs which are composed of minute primary particles and crystallites. The average size of pseudomorphs, estimated to be $0.5\text{ }\mu\text{m}$ by TEM observation, agrees with that of the secondary particle size. It is thought that the pseudomorphs retain their original hexagonal shapes at this temperature, since the distribution curve of secondary particle sizes remains unchanged regardless of an increase in the heating time. Although it is presumed that the cracks may propagate through the pseudomorphs as the agglomeration of primary particles proceeds [15, 18], the crack size seems to be too small to collapse the pseudomorphs.

The tap density of MgO powder heated for 300 min becomes higher than those for 10 and 60 min. A comparison of the results of tap density with those of primary particle growth suggests that the agglomerate density may be enhanced by expelling the pores in pseudomorphs due to the rearrangement and coarsening of primary particles, because the theoretical apparent porosity of initial MgO would be about 54% [15];

moreover, since the amount of chemically-adsorbed water is reduced with increasing the heating times [1, 19], the weakening of linkage between pseudomorphs makes their rearrangement easy. The agglomerate strength is estimated to be about 70 MPa independent of the heating time; it is inferred that the bonding strength of primary particles in pseudomorphs remain unchanged, probably because a mass transfer is restricted chiefly to the particle surface [16].

4.2. Agglomeration process at 800°C

The agglomeration behaviour of crystallites and primary particles at 800°C is similar to that at 600°C, judging from the results of *DA-CP* value; the coherent crystallites coalesce within the heating time of 60 min and then the primary particle growth proceeds.

As shown in the preceding paper [14], the fragmentation and agglomeration of pseudomorphs occur in the range of 650 to 850°C. This phenomenon can also be verified in this paper not only by the direct observation but also by an increase in secondary particles with an average size of 1.4 μm in MgO powders heated for 300 min. Fragmentation may occur by the propagation of cracks through pseudomorphs; it seems that the strains enough to collapse the pseudomorphs are generated at the critical size as the coherent primary particles grow [20].

The tap density of MgO powder is raised by extending the heating time from 10 to 60 min, which suggests that the pores within the pseudomorphs and fragments may be expelled by the coalescence and coarsening of primary particles. The agglomerate strength, estimated to be about 100 MPa, is independent of heating time. This value is somewhat higher than that of the powder heated at 600°C; the bondings of crystallites and of primary particles in agglomerates may be reinforced by an activated mass transfer.

4.3. Agglomeration process at 900°C

TEM observation reveals that vermicular particles with large pores are present after heating the MgO powder for 300 min, which suggests that the crystallite and primary particle growth bring about the pore migration and result in the pore coalescence; this assumption has already been verified by the fact that the pore-size distribution at 900°C shifted towards values larger than those at 600°C [14]. The primary particle and crystallite growth may increase the contact area and, therefore, accelerate the mass transfer not only on the surface but also through the bulk of MgO at this temperature [21]. It does not seem that most of these pores are expelled from the system during heating, since the tap density remains unchanged through various heating times.

A gradual reduction of the secondary particle size with increasing the heating times suggests that the fragmentation of agglomerates proceeds with the crack growth, because the rearrangement of primary particles brings about the coalescence of pores [14].

4.4. Agglomeration process at 1200°C

The agglomerate properties of MgO powders at this temperature are altered at the heating time of 240 min.

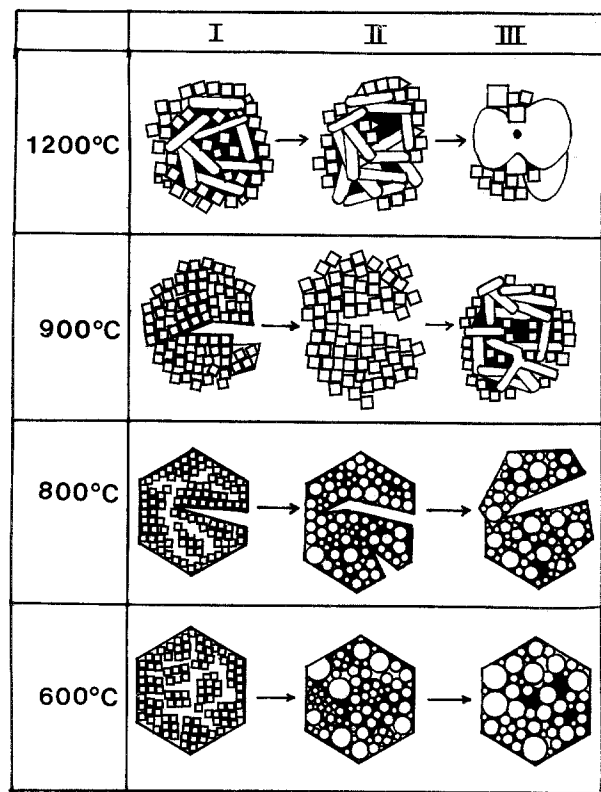


Figure 10 Model for agglomeration process of MgO powder obtained by decomposing the $\text{Mg}(\text{OH})_2$.

Within this heating time, the coherent crystallites show the coalescence inside of a primary particle because the *DA-CP* value decreases from seven to three.

On continuation of heating from 240 to 300 min, primary particle growth predominates over crystallite growth, as the sudden rise in *DA-CP* value from three to 23 indicates; consequently, the size of primary particles, estimated to be about 0.7 μm, becomes almost the same as that of secondary particles. It is inferred that primary particles may grow rapidly by the entrapment of pores within them. This assumption is supported by the experimental results obtained by the examination of MgO powder heated for 300 min: (1) SSA rises from 2.3 to 12.1 m² g⁻¹ by grinding and (2) the tap density becomes higher than those heated for 10 and 60 min. When the MgO powder heated for 300 min is continuously tapped, the density is raised suddenly at around 500 taps; this phenomenon can be interpreted as a packing of smaller agglomerates between larger agglomerates, which demonstrates that the surface smoothing due to sintering makes their packing easy.

Figure 10 summarizes the agglomeration process of MgO particles derived from $\text{Mg}(\text{OH})_2$. At 600°C, coherent crystallites show the coalescence within the pseudomorphs (Stage I → II); the primary particles start to grow after the crystallites have coalesced (Stage II → III). At 800°C, an agglomeration of crystallites and primary particles creates the cracks, resulting in the fragmentation of pseudomorphs (Stage I → II → III). At 900°C, the crystallite and primary particles in fragments grow with the coalescence of pores (Stage I → II → III). At 1200°C, the crystallite

and primary particle growth bring about the pore migration (Stage I → II) and then the entrapment of pores within them (Stage II → III).

5. Conclusions

The agglomeration process of MgO powder derived from Mg(OH)₂ was investigated by fixing the temperatures at 600, 800, 900 and 1200°C; these temperatures were chosen as representative of the four regions; below 600°C, 650 to 850°C, 850 to 1050°C, 1050 to 1200°C. The results obtained were as follows:

1. At 600°C, crystallites were agglomerated and then coalesced during heating within 60 min; on further heating, the primary particles, which consisted of crystallites, grew rapidly. The original Mg(OH)₂ framework, composed of minute crystallites and primary particles, still remained as secondary particles in the powder.

2. At 800°C, the crystallite and primary particle growth behaviours were similar to those at 600°C; the pseudomorphs had disintegrated into a pile of fragments.

3. At 900°C, the crystallite and primary particle growth were brought about by the pore coalescence; some fragmentation of agglomerates proceeds with the crack growth.

4. At 1200°C, the crystallite and primary particle growth proceeded with the migration of pores; on heating beyond 240 min, the crystallites and primary particles grew rapidly due to the entrapment of pores within them.

5. The agglomeration process of MgO powder derived from Mg(OH)₂ at fixed temperature could be expressed as schematic diagrams; furthermore, each process could be divided into three stages.

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