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Grain Size and Form of Magnesium Oxides

Obtained from Different Magnesium Carbonates

at Different Calcination Temperatures

Hiroshi KUNO*

Yoshio HAYASHI**

Abstract

Magnesium oxides are prepared by calcinating the fine plate-like basic magnesium carbonate and the coarse rod-like magnesium carbonate at 600° 800°, 1000°, 1200° and 1400° C.   The effects of the sizes and shapes of the carbonates and the effects of the calcination temperature on the properties of magnesias are studied by the observation with the electron microscope and by the measurements of iodine adsorptions, apparent densities and solubilities in the acetic acid.

The growth of the sizes of the primary particles and the decrease of the specific surfaces of the magnesias are occured with the raise of the calcination temperature. Above 1000° C., the characteristic cubic crystals of the magnesium oxide are observed.   The sintering of the magnesia particles takes place above 1200° C..

The primary particles of the magnesia form a kind of skeletons, i. e. the secondary particles, and they retain the sizes and shapes of the original carbonates, therfore the apparent densities of the magnesias are close to that of the carbonates from which they were prepared.

I Introduction

Many works on the effects of the calcination temperature on the properties of the active magnesia have been reported.   But since these works have been concerned with the active magnesia, the calcination temperatures were always confined under 1000° C. and little has been done with the effects of the calcination temperature above 1000° C. on the sizes and shapes of the magnesia particles.   Moreover, in these works the basic magnesium carbonates were used, and no interest was paid to the other magnesium carbonates.   In this work, we change the calcination temperature from 600° to 1400° C., and observe its effects on the sizes,

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shapes and specific surfaces of the magnesia paticles. At the same time, the effects of the magnesium carbonates are studied by using two kinds of them.

II Experimental

Preparation of magnesium carbonates. —— Two kinds of magnesium carbonate are prepared by mixing 10% aqueous solution of magnesium sulfate and that of sodium bicarbonate at two different temperatures of 50° and 70° C.. These two solutions are brought to the reaction temperature and then are mixed at the ratio of $4NaHCO_3$ to $1MgSO_4$. The mixtures are stirred 2 hrs. at the reaction temperature and are kept still about an hour at the same temprature, and the precipitates are washed several times with distilled water by decantation and are separated from the liquids by filtration. The greater parts of these precipitates, which will be used for the preparation of the magnesium oxides, are dried by an infra-red ray lamp and are kept in a desiccator, but a part of the precipitates is washed with ethanol and is dried in vacuum at the room temperature.

The shapes of these carbonates prepared at 50° and 70° C. are shown in Fig. 1_a and 1_b respectively by light and electron microphotographs. The former is coarse and has a rod-like shape of 15μ in average length and 2μ in average diameter. The latter is finer than the former and has a plate-like shape of about 30 mμ in thickness and 1μ in diameter.

These carbonates are studied by X-ray diffraction and the changes of weight due to those of temperature, seen in Fig. 2, are measured by a thermobalance. From Fig. 2 and by comparing the X-ray data with those of Hanawalt and others,[1] we find that these carbonates prepared at 50° and 70° C., dried with ethanol, are $MgCO_3 \cdot 3HO_2$ and $5MgO \cdot 4CO_2 \cdot 5H_2O$ respectively. The carbonates dried by the infra-red ray lamp, however, both give somewhat different X-ray data from those of above given carbonates, and the one prepared at 50°C. is considered to have the component of $MgCO_3 \cdot H_2O$ according to H. Menzel and others[2] and from the results given in Fig. 2.

Preparation and measurements of magnesium oxides. —— Two series of magnesium oxides are produced by the calcination of the magnesium carbonates dried with the infra-red ray. Series 'A' is produced from the carbonate prepared at 50°C. and series 'B' from that prepared at 70°C.. Four kinds of magnesia are prepared by the calcination of the two kinds of magnsium carbonate at 600° C., 1 hr. and 800°C., 1 hr., and eight more kinds of magnesia are produced by calcination again at 800°C., 1 hr.; 1000°C., 1 hr. ; 1200°C., 1 hr. and 1400°C., 1 hr. the two kinds of magnesia prepared at 800°C. before.

1) J. D. Hanawalt, H. W. Rinn and L. K. Frevel, Ind. Eng. Chem., Anal. Ed., **10**, 466 (1938)

2) H. Menzel and A. Brückner, Z. Elektrochem., **36**, 63 (1930).
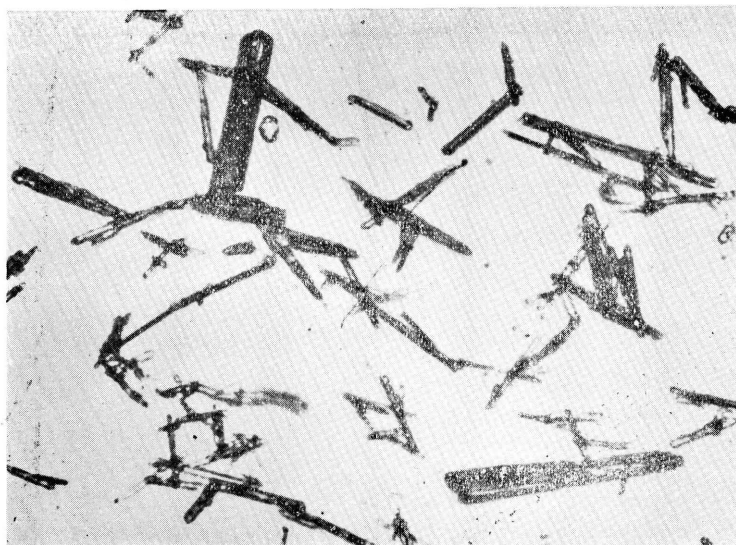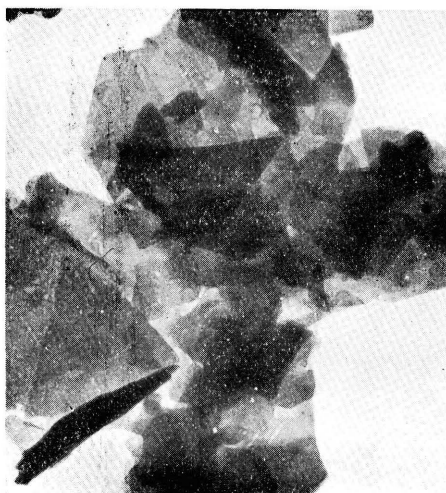   H. Menzel, A. Brückner and H. Schulz, Z. Elektrochem., **36**, 188 (1930)

Fig. 1a. Microphotograph of the magnesium carbonate prepared at 50°C. (×200).

Without shadowing.

Chromium shadowed.

Fig. 1b. Electron microphotographs of the magnesium carbonate prepared at 70°C. (×20,000).

The magenesias are observed with electron microscope and X-ray diffraction patterns of them are taken. The measurements of iodine adsorption are essentially the same as that of A. C. Zettlemoyer and W. C. Walker[3] except that we use 0.01N iodine in benzene instead of 0.1N iodine in CCl_4. The apparent densities of
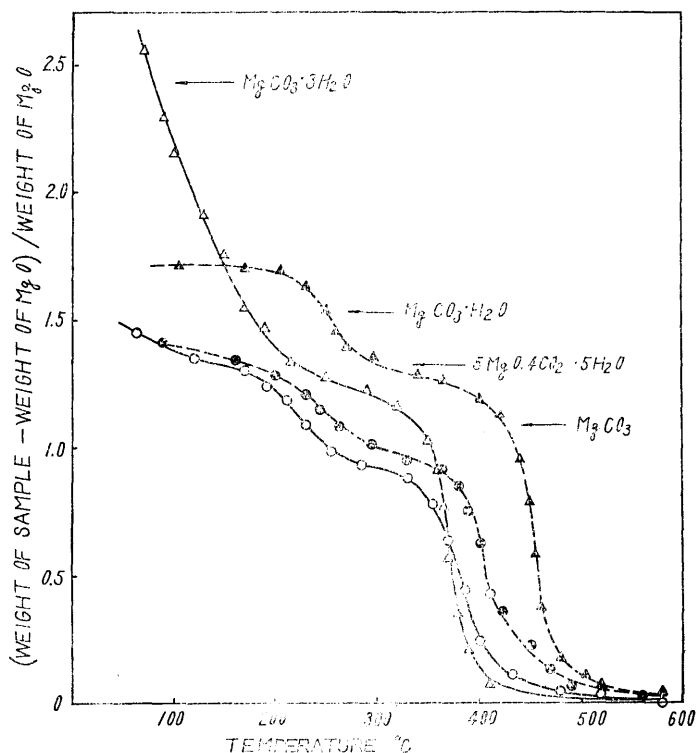
Fig. 2. The weight changes of magnesium carbonates due to the changes of the temperature

The weight of MgO means the final weight of the sample at 700°C.
The arrows show the theoretical values corresponding to the chemical formulae given there.

△; Magnesium carbonate prepared at 50°C., dried with ethanol.

▲; Magnesium carbonate prepared at 50°C., dried with infra-red ray.

□; Magnesium carbonate prepared at 70°C., dried with ethanol.

●; Magnesium carbonate prepared at 70°C., dried with infra-red ray.

3) A. C. Zettlemoyer and W. C. Walker, Ind. Eng. Chem., 39, 69 (1947)

4) H. Kuno and Y. Hayashi, This Journal, 6, No. 22, 59 (1953)

magnesia are measured by the apparatus we devised,[4] with the glasstube of 13.5 mm. in diameter. The solubilities of the magneias in 7×10^{-3}N acetic acid at 30°C. are also measured.

III. Result and discussion

Electron microphotographs of magnesias of series 'A' and 'B' are given in Fig.3 and 4 respectively. These microphotographs clearly show the skeletons of carbonates which are composed of primary particles of magnesias, therefore we can easily expect the effects of the shapes of the carbonates on the shapes of the secondary particles of these magnesias. The primary particles are small and spherical at low temperatures of calcination, they grow, however, as the calcination temperature is raised, and we imagine the occurrence of the rearrangement of molecules from the appearance of beautiful cubic crystals of magnesium oxide in Fig. 3 (e), (f) and Fig. 4 (d), (e) and (f). The connection and rounding up of edges of the primary particles in Fig. 3 (f) and Fig. 4 (e), (f) may be due to the sintering of these particles.

The apparent densities, the solubilities in 7×10^{-3}N acetic acid and the specific surface areas calculated from the iodine adsorption are given in Table 1. The specific surface areas are calculated assuming that the area occupied by the iodine molecule is 35.33 Å². [5]

Table 1

| Calcination temperature °C.	Apparent density g./cm.³		Solubility in 7×10^{-3}N acetic acid 30°C. g./l		Specific surface area by I_2 adsorption m.²/g.	
	A°	B	A	B	A	B
600	0.318	0.127	0.194	0.198	47.3	26.9
800	0.417	0.166	0.185	0.211	8.97	7.95
800+800*	0.431	0.171	0.229	0.225	10.0	11.3
800+1000	0.458	0.233	0.220	0.406	4.66	4.27
800+1200	0.475	0.312	0.178	0.239	3.41	0.59
800+1400	0.499	0.454	0.212	0.214	0.81	0.26
magnesium carbonate**	0.444	0.172				

° A and B mean the serieses of magnesias which are produced from the magnesium carbonates prepared at 50° and 70°C..

* 800+800 means to calcinate again at 800°C. the magnesia which is produced by the calcination of the carbonate at 800°C.. 800+1000means the recalcination at 1000°C..
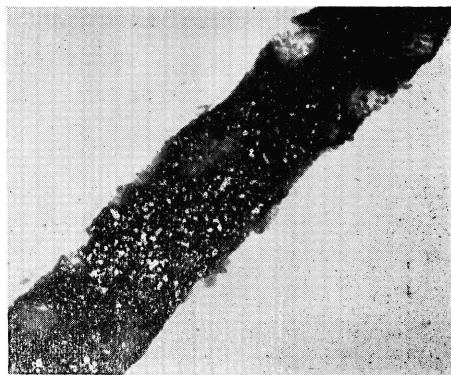
** Magnesium carbonates from which the magnesias are produced.

The apprent densities of the magnesias of series 'A' and 'B' are quite different, and their values are colse to the values of the original carbonates from which
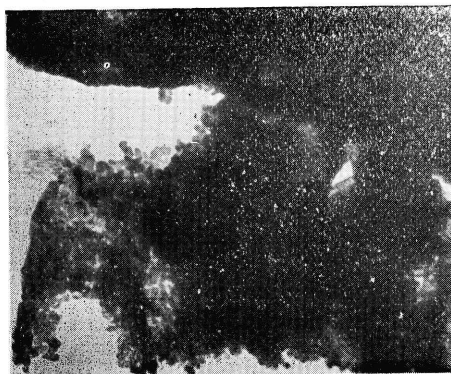
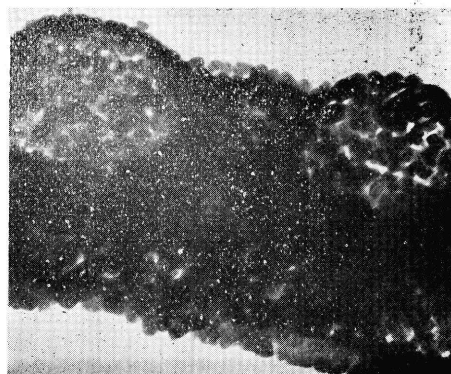5) W. C. Walker and A. C. Zettlemoyer, J. Phys. Chem., 57, 182 (1953)
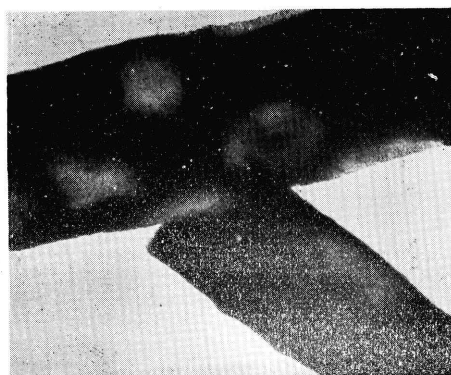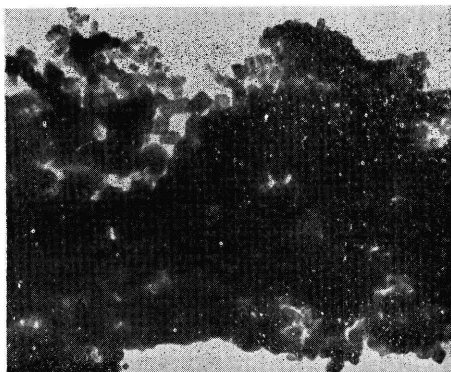
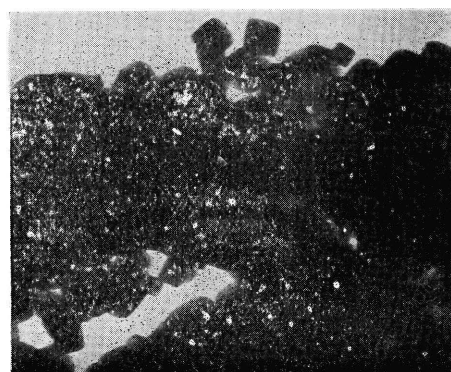a) Calcinated at 600°C., 1hr.

b) Calcinated at 800°C., 1hr.

c) Calcinated (b) again at 800°C., 1hr.

d) Calcinated (b) again at 1000°C., 1hr.
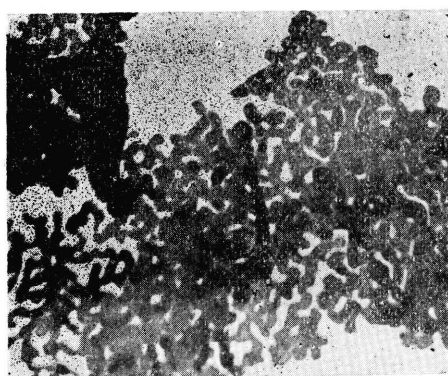
e) Calcinated (b) again at 1200°C., 1hr.
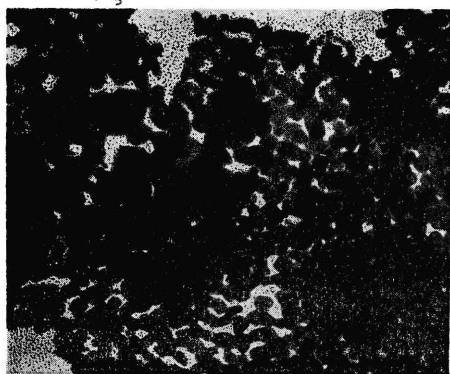
f) Calcinated (b) again at 1400°C., 1hr.

Fig. 3. Electron microphotographs of the magnesium oxides produced by the calcination of magnesium carbonate prepared at 50°C., (×20,000).
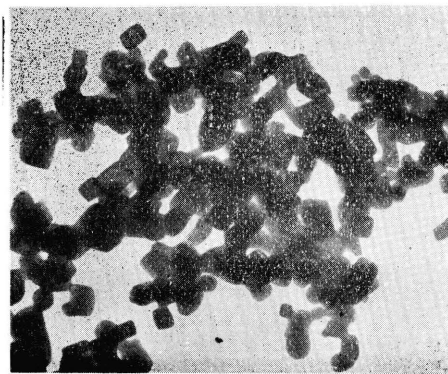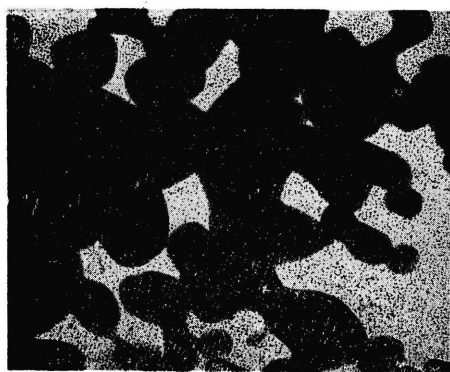
a) Calcinated at 600°C., 1hr.

b) Calcinated at 800°C., 1hr.

c) Calcinated (b) again at 800°C., 1hr.

d) Calcinated (b) again at 1000°C., 1hr

e) Calcinated (b) again at 1200°C., 1hr.

f) Calcinated (b) again at 1400°C., 1hr.

Fig. 4. Electron microphotographs of the magnesium oxides produced by the calcination of magnesium carbonate prepared at 70°C. (×20,000).

they were produced.   The effects of the calcination temperature are smaller in these cases than the effects of material particles except at the cases of strong calcination.   This phenomenon agrees with the fact that the shapes of the carbonates are retained in the shapes of the secondary particles of magnesias, which we found in the electron microphotographs.

No significant results are obtained in the solubility data.

The specific surface areas of the magnesias decrease with the increase of the calcination temperature.   This tendency can be found likely in both series of magnesias, but in the series 'B' the same calcinating effects appear at lower temperature than in the series 'A'.   This difference of the two serieses, which also can be expected from the nature of the carbonates seen in Fig. 2, is considered mainly due to the difference of the particle sizes of the two carbonates used.   The large decrease of the specific surface areas at 1400°C, in series 'A' and at 1200°C. in series 'B' may be presented by the sintering of magnesia particles.

The mean diameters of the magnesia partcles are calculated from the specific surface areas assuming the particles are cubic.   The results are given in Table 2

Table 2.   Particle diameter of MgO

Calcination temperature °C	Diameter calculated from specific surface area* mμ		Diameter measured by electron microscope mμ	
	A	B	A	B
600	3.4	6.0	10 − 20	10 − 25
800	18.1	20.4	20 − 50	30 − 80
800+800	16.2	14.3	30 − 50	30 − 80
800+1000	34.7	38.0	40 − 90	50 − 150
800+1200	47.5	277.	50 − 120	100 − 300
800+1400	201.	625.	100 − 230	150 − 350

* The shape of particle is assumed to be cubic.

with   the particle diameters which   are measured from the electron microphotographs.   The diameters calculated from the specific surface areas are smaller than those values measured from the electron microphotographs at the temperatures under 1200° and 1000°C. in series 'A' and 'B' respectively.   But at higher calcination temperatures than these temperatures this relation is reversed, and this reversal seems to be occured by the sintering of the magnesia particles.   The diameters of magnesia particles calcinated at 600°C., measured from the half width of the X-ray diffraction lines by the method of L. S. Birks and H. Friedman,[6] are 10.1 and 9.2 mμ for series 'A' and 'B' respectively, but for the other magnesias the mesurments are not successful.

6) L. S. Birks and H. Friedman, J. App. Phys., 17, 687 (1946)

Acknowledgement