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SINTERING OF MAGNESIUM OXIDE PREPARED BY ALKOXY-METHOD

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Magnesium oxide was prepared by the alkoxy-method, and its sinterability was studied. Compact specimens exceeding 96 % of bulk density were obtained by sintering at 1200 °C for 3 h.

It is well known that the reactivity of solid changes remarkably according to their preparation conditions. We have studied the properties and sintering of various powders prepared by the alkoxy-method [1)-6)]. The present investigation deals with the effects of calcining temperature and time on the sintering of the magnesium oxide(MgO) powders prepared by the thermal decomposition of magnesium hydroxide($Mg(OH)_2$) derived from alkoxide.

The starting material was synthesized by heating magnesium foil of 99.99 % purity in an excess isoamyl alcohol containing a small amount of ethyl bromide at 85 °C for 7 h [5),6)]. The obtained magnesium isoamyloxide was hydrolyzed by pouring slowly into water at 90 °C. X-Ray diffraction patterns showed that the resulting product was $Mg(OH)_2$. Thermal analysis of the powder at the heating rate of 10 °C/min showed that the dehydration was completed at 440 °C. Gradual weight loss of 3.45 % was observed between 440 and 930 °C. This would be attributed to the liberation of alcoholic residue occluded in the derived powder. Loose $Mg(OH)_2$ powders were calcined in air for 1 to 3 h at the temperature range of 400 to 1200 °C. The calcined powders were compacted into disk at 3 ton/cm^2 using water as a binder. The compacts were sintered in air for 1-5 h at 1200 °C and 1300 °C. Heating rate was 200 °C/h. Relative densities were calculated using 3.58 g/cm^3 [7)] for the bulk density of MgO.

Electron micrographs of the MgO powders calcined at 400 to 1200 °C for 1 h are shown in Fig. 1. Calcining at 400 °C gave angular particles. The aggregates of small particles were formed at 600 °C and 800 °C. At 1000 °C particles became roundish and formed larger aggregates, and particle growth was observed at 1200 °C.

X-Ray diffraction peaks of MgO showed a remarkable line broadening. The mean

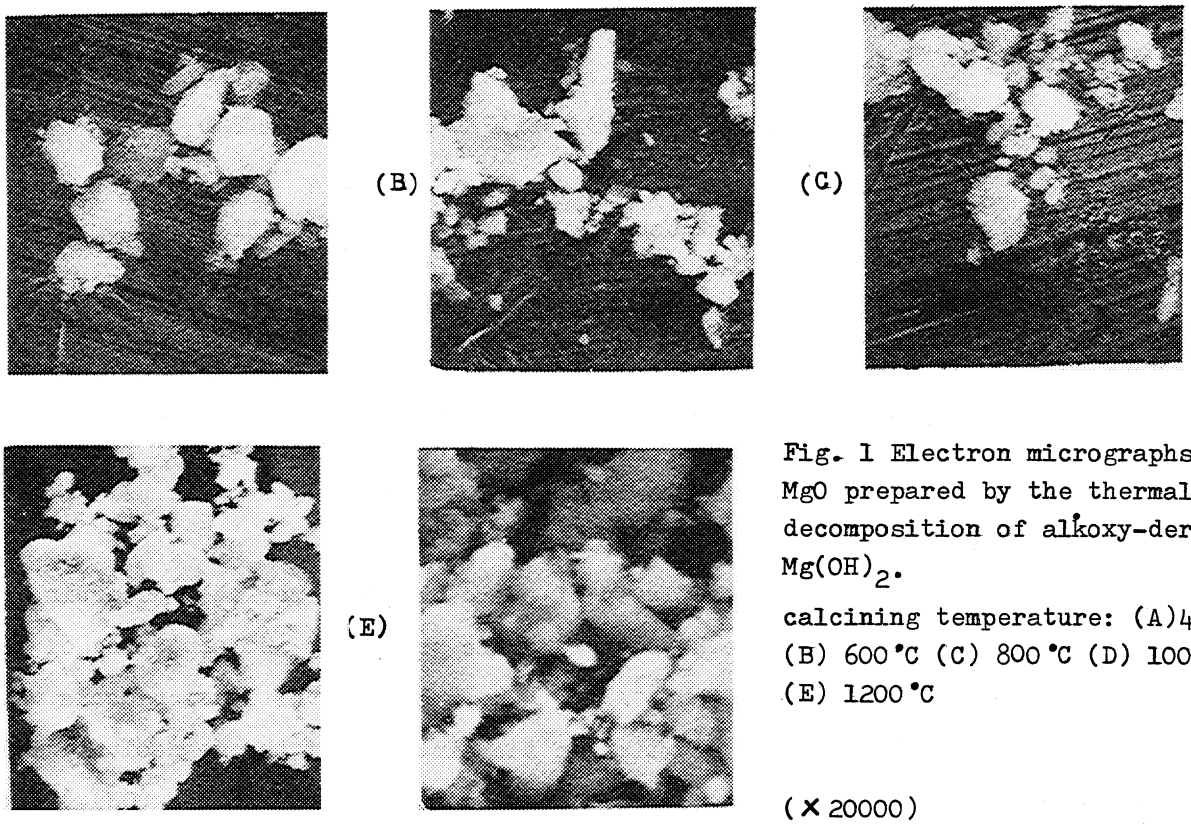

Fig. 1 Electron micrographs of MgO prepared by the thermal decomposition of alkoxy-derived $Mg(OH)_2$.
calcining temperature: (A) 400 °C (B) 600 °C (C) 800 °C (D) 1000 °C (E) 1200 °C
(× 20000)

fluctuation of the interplanar spacing, $\Delta d/d$, was estimated from the slope of the $\beta\cos\theta$ vs. $\sin\theta$ curve and the size of the crystallite was determined by extrapolating $\beta\cos\theta$ values to $\sin\theta=0$ [8]. Quartz was used for calibration as a standard material. Judging from the results summarized in Table 1, the X-ray line broadening is presumably due to the small crystallite size as well as to the lattice distortion. A large size of the crystallite at 1200 °C is consistent with the observation by the electron microscope. A fairly large fluctuation of the interplanar spacing was observed in the temperature range of 400 to 1000 °C.

Figure 2 shows the effects of calcining temperature on the green and sintered densities of the MgO compacts prepared by various methods [9),10]. It is seen that the sintered density of MgO prepared by the present method is higher than that of MgO prepared from reagent-grade $Mg(OH)_2$. The optimum calcining

Table 1 Crystallite size and $\Delta d/d$ of MgO calcined at various temperatures and time.

calcining temp.(°C), time(h)	crystallite size(Å)	$(\Delta d/d)\times 10^3$
400 , 1	290	4.64
600 , 1	320	4.46
800 , 1	360	3.57
800 , 2	390	3.31
800 , 3	420	2.95
1000 , 1	600	2.58
1200 , 1	1200	0

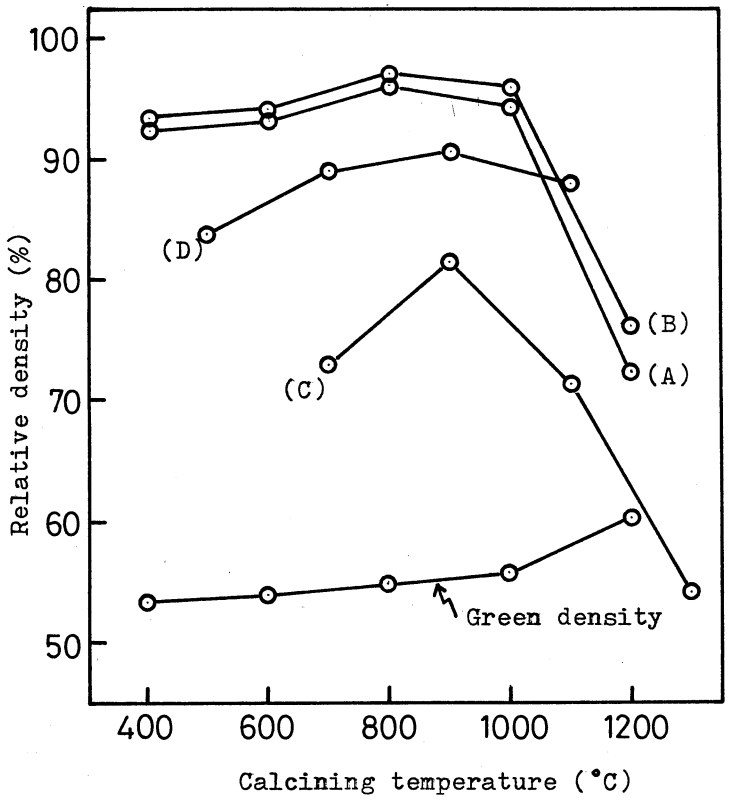

Fig. 2 Effect of calcining treatment on the green and sintered densities of the MgO compacts.

(A) present study 1200°C, 3 h
(B) present study 1300°C, 3 h
} from alkoxide

(C) Hamano et al. 1400°C, 3 h
(D) Livey et al. 1600°C, 1 h
} from reagent-grade $Mg(OH)_2$

MgO powders used in the present study were calcined at each temperature for 1 h.

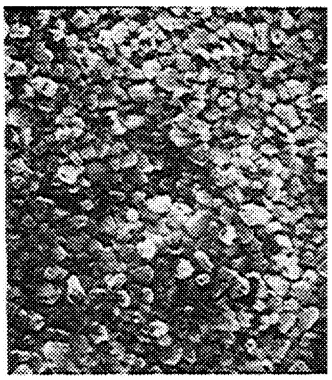

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Fig. 3 Electron micrograph of MgO compact sintered at 1200°C for 3 h.
800°C, calcined for 2 h

temperature for obtaining high sintered density was at 800 to 1000°C. Figure 3 shows an electron micrograph of the compact sintered at 1200°C for 3 h after calcining at 800°C for 2 h.

According to Wermuch and Knapp [11], the initial sintering of MgO is governed by grain-boundary diffusion of oxygen ions. The alcoholic hydrocarbon occluded in powders or free carbon produced by decomposition may react with oxygen of MgO at the surface, resulting in the evolution of CO and/or CO_2 and H_2O. As a result, many oxygen vacancies in non-equilibrium would be produced in the vicinity of grain boundary, and the sintering of MgO could be accelerated remarkably. Such vacancies will probably be responsible for the observed large $\Delta d/d$ values of MgO prepared by the alkoxy-method. The details of the sintering mechanism are now under investigation and will be reported

soon.

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