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FORMATION OF FORSTERITE($2MgO \cdot SiO_2$) FROM THE MIXTURE PREPARED BY ALKOXY-METHOD

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Forsterite($2MgO \cdot SiO_2$) was formed at low temperatures by heating the mixed powders prepared by the simultaneous hydrolysis of magnesium and silicon alkoxides.

It is known that the reactivity of solids changes remarkably according to their preparation conditions. The authors have studied the properties and sintering of various powders prepared by alkoxy-method.[1)-4)] The purpose of this paper is to show the formation of forsterite($2MgO \cdot SiO_2$) at low temperatures by heating the mixed powders prepared by the simultaneous hydrolysis of magnesium and silicon alkoxides.

Silicon ethyloxide used in this experiment was of the guaranteed reagent. Magnesium isoamyloxide was prepared by the reaction of magnesium metal and isoamyl alcohol with a small amount of ethyl bromide as a catalyst.

$$Mg + 2C_5H_{11}OH \xrightarrow[130\,^\circ C,\,7\ h]{C_2H_5Br} Mg(OC_5H_{11}OH)_2 + H_2$$

The purity of magnesium metal used in the reaction was four nine. Isoamyl alcohol was purified by fractional distillation of the guaranteed reagent.

A mixture of these alkoxides with the mole ratio of Mg^{2+}/Si^{4+} = 2:1 was prepared, and then poured into aqueous solution of ammonia at about 30 °C. The temperature was slowly raised up to 90 °C with stirring. The mixed powders hydrolyzed in this way were washed repeatedly with hot distilled water and dried at 120 °C. The average particle size of the mixed powders was approximately 100 - 200 Å.

The TG of the mixed powders was carried out in air from room temperature to 1000 °C(Fig. 1). The weight loss of 40.3 % up to 670 °C is attributed to the loss of absorbed H_2O, NH_4OH, CO_2 and organic residue from the parent alcohol. DTA of the mixed powders was also performed. An exothermic reaction was observed between 720 and 810 °C. This reaction was found to be the crystallization of $2MgO \cdot SiO_2$ from an amorphous phase

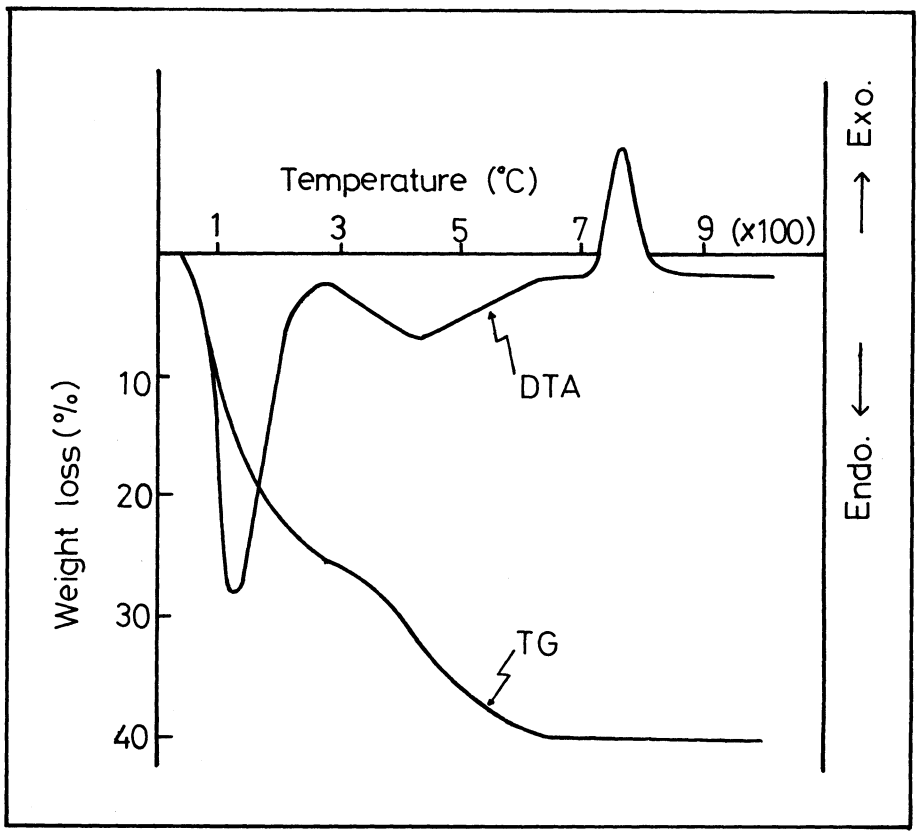

Fig.1 TG and DTA of alkoxy-derived $2MgO \cdot SiO_2$ powder. Sample weight: 30mg, Heating rate: 10°C/min.

from the results of X-ray diffraction(Fig. 2).

Figure 2 shows the variation of X-ray diffraction patterns of alkoxy-derived $2MgO \cdot SiO_2$ with increasing temperature. The mixed powders as a raw material were amorphous and no significant changes were observed up to 650 °C. The peaks corresponding to $2MgO \cdot SiO_2$ began to appear after the heat treatment at 680 °C for 15 min, and the intensity increased rapidly with increasing temperature. No other peaks were identified except for the $2MgO \cdot SiO_2$ spectrum.

Figure 3 shows the rate of $2MgO \cdot SiO_2$ crystallization determined for four different temperatures of 680, 710, 740 and 770 °C. The mixed powders were pre-heated at 200 °C for 15 min. The yield of crystallization of each specimen was determined from the height of 112 reflection which is the strongest peak of the $2MgO \cdot SiO_2$ spectrum in X-ray diffraction. Well-crystallized $2MgO \cdot SiO_2$ specimen was obtained by heating of the alkoxy-derived mixed powders at 1400 °C for 5 h. Calcium fluoride was used as a stand-

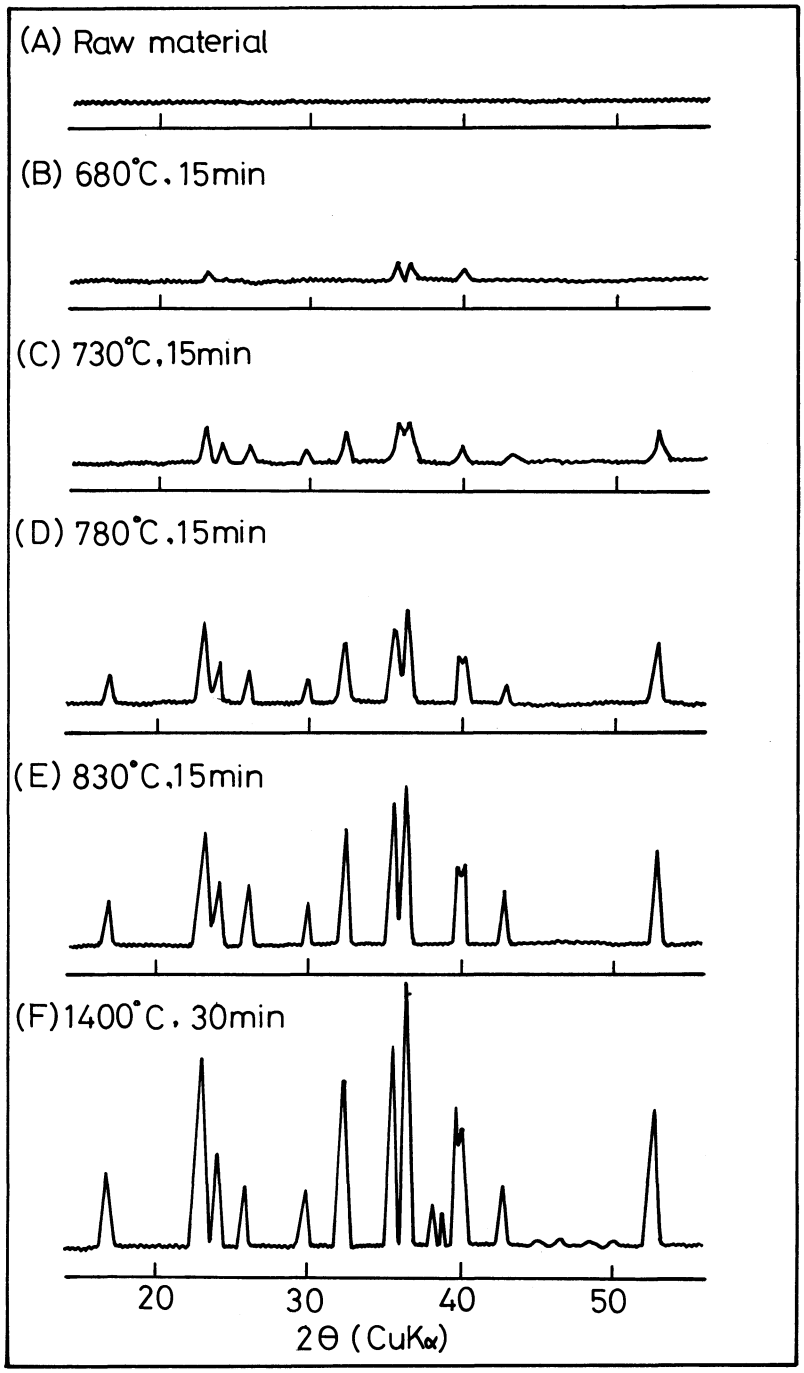

Fig.2 X-ray diffraction patterns for alkoxy-derived $2MgO \cdot SiO_2$ powder.

Heating rate : 300°C/hr

ard material. As shown in Fig. 3, the yield of crystallization is strongly dependent on temperature and heating time. Above 800 °C the crystallization proceeded rapidly. Attempts were made to fit the results to many kinetic laws. The data can be interpreted in terms of the second-order rate law, as a special case[5] of the treatment given by Avrami.[6] Figure 4 shows the second-order plots of f/1-f against t, where f is the rate of the crystallization and t is the time. The values of the activation energies calculated from the Arrhenius plots were 42.5 kcal/mol and 32.4 kcal/mol for initial and final stages, respectively. These activation energies represent those for establishing active growth centers.

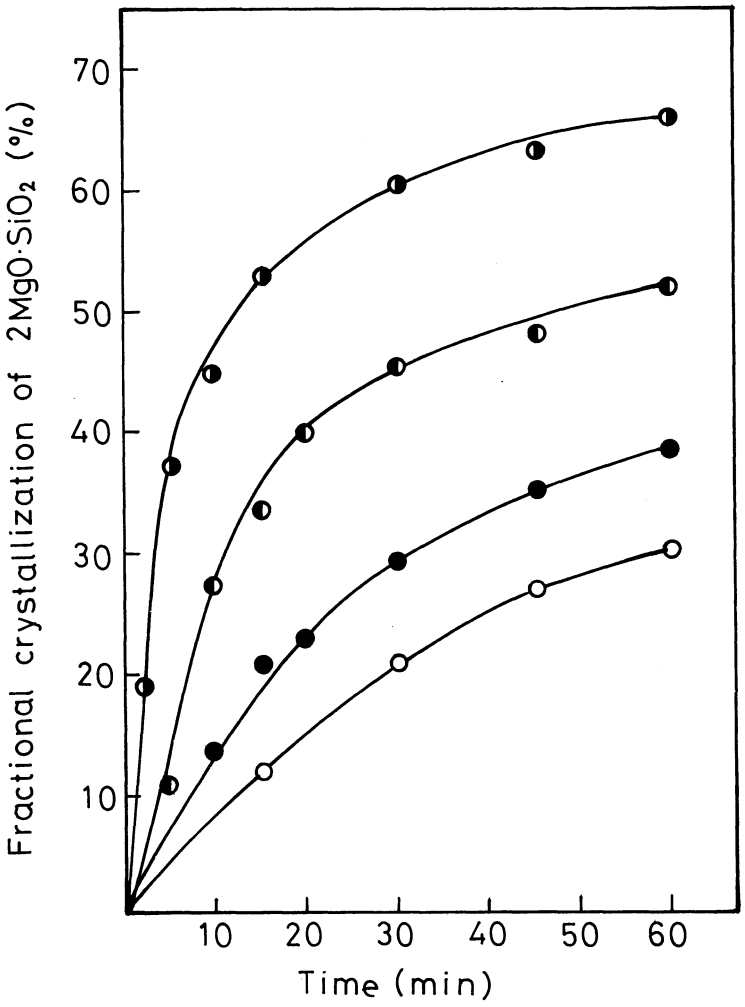

Fig.3 Crystallization of $2MgO \cdot SiO_2$ as a function of time at different temperatures.
○: 680°C, ●: 710°C, ◐: 740°C, ◑: 770°C

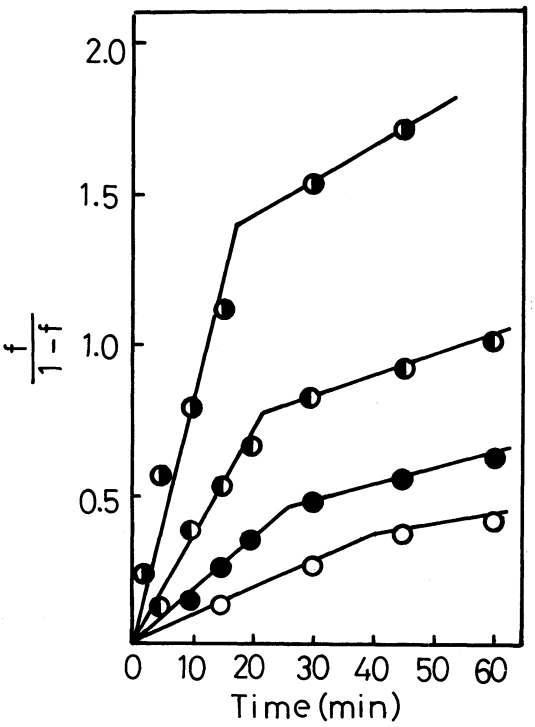

Fig.4 Second-order plots of the data of fig.3.
○:680°C ●:710°C
◐:740°C ◑:770°C

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