Journal of Thermal Analysis Vol. 33 (1988) 909–914

HIGH-TEMPERATURE SYNTHESIS OF MAGNESIUM SILICATES FROM SOLID MIXTURES OF SiO_2 AND VARIOUS MAGNESIUM COMPOUNDS

H.-J. Huhn

RESEARCH INSTITUTE OF MINERAL PROCESSING OF THE ACADEMY
OF SCIENCES OF THE G.D.R., STRASSE DES FRIEDENS 40,
FREIBERG, 9200, G.D.R.

For many years, the high-temperature synthesis of magnesium silicates from a magnesite–quartz sand mixture has been the basis for the production of enstatite and the subsequent manufacture of steatites for the ceramics industry of the G.D.R. It is now shown that, in principle, mixtures of other magnesium compounds with SiO_2 can also be transformed to magnesium silicate phases.

Depending on the mechanical and thermal conditions chosen, different reactive intermediates are formed which, after ceramic firing, are responsible for the differences within the phase composition.

Thermoanalytical methods are well suited to compare the solid-state reactivities of various mixtures.

During the high-temperature solid-state reaction of MgO and SiO_2, a thin layer of metasilicate is formed first, by the diffusion of Mg^{2+} ions to the SiO_2 phase boundary, preceding a thicker growing reaction front of forsterite. At a low, nearly constant amount of metasilicate, the forsterite content increases until the free MgO is consumed. Metasilicate is then formed, at a clearly lower velocity [1].

The reaction equations are:

$$MgO + SiO_2 \rightarrow MgSiO_3 \xrightarrow{MgO} Mg_2SiO_4 \xrightarrow{SiO_2} 2\,MgSiO_3$$

For a $MgCO_3$–SiO_2 mixture ground in a vibration mill and heated to various temperatures, Fig. 1 shows the phase amounts, which were determined by X-ray diffraction. It can be seen that, from about 950° onward, forterite (F) is first formed from periclase (P) and quartz (Q); from 1200° on, this reacts further with quartz (Q) and cristobalite, to give the lower magnesium-containing modifications, protoenstatite (PE), enstatite and clinoenstatite (E). We deal here with the synthesis of magnesium silicates in which MgO is substituted by magnesium salts which form MgO during thermal treatment.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

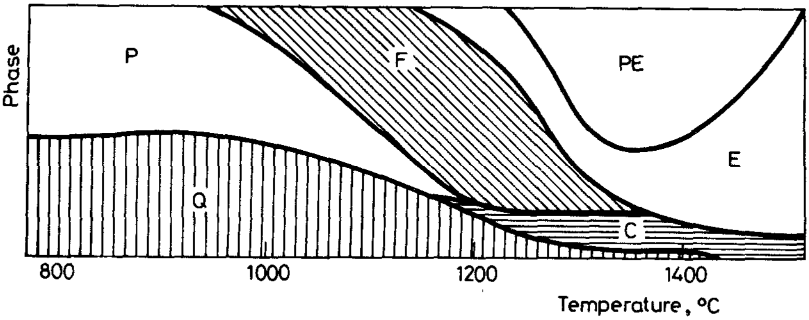

Fig. 1 Schematic representation of the phase composition of a $MgCO_3$–SiO_2 mixture annealed four hours in the muffle furnace

Experimental

In order to follow the reactions taking place during annealing and to evaluate the solid-state reactivity, thermoanalytical methods were applied under the following fixed conditions:

Thermoanalyser TA 1 (Mettler):

Weighed portions of 100 mg powder in a macrocrucible, heating rate 6 deg min^{-1} in flowing air atmosphere, sensitivities for TG 1 = 100 mg, DTG = 10 mg min^{-1} and DTA = 200 μV.

Q-Derivatograph (MOM):

Weighed portions of 230–250 mg in a labyrinth crucible, quasi-isothermal operation, max. 0.6 mg min^{-1} and max. 2.5 deg min^{-1} sensitivities for TG = 200 mg and DTA = 250 μV.

For determination of the real structure and the phase composition, a PW 1025 X-ray diffractometer (Philips) was used with CuK_α radiation and a graphite monochromator in a stepping operation at 0.5 °ϑ min^{-1}.

A good survey of the progress of the reaction is also given by a chemical method [2] based on the principle of the different solubilities in NH_4Cl and HCl.

Results

As can be seen from the results in Table 1, with the intense comminution in the vibration mill a reduction in the primary particles occurs. During mixture grinding,

Table 1 Influence of the addition of quartz sand and vibration grinding on the primary particle size determined by X-ray diffraction and on the thermal decomposition of magnesite after dynamic heating in the Thermoanalyser TA 1

Material	Grinding time	Primary particle size, nm		MgO amount formed, % at	
		$MgCO_3$	SiO_2	500 °C	600 °C
$MgCO_3$		43	—	1.9	53.2
$MgCO_3+SiO_2$		45	101	2.1	56.7
$MgCO_3$	5 min	33	—	7.2	59.7
$MgCO_3$ + 5 min SiO_2	5 min	33	82	8.3	76.4
$(MgCO_3+SiO_2)$	5 min**	27	85	11.9	86.0
$MgCO_3$	20 min	25	—	10.5	70.0
$(MgCO_3+SiO_2)$	20 min**	16	70	18.6	95.2

* each component ground separately
** ground after mixing of components

the magnesite particles are more stressed by the relatively hard quartz grains acting as additional grinding bodies. In parallel to the destruction of the magnesite lattice, an increase in solid-state reactivity can also be observed. The highest decomposition rate is found for binary mixtures ground together.

When the $MgCO_3$–SiO_2 mixtures are annealed to more than 1000°, magnesium silicate formation can be increasingly observed. The less reactive powder mixtures exhibit distinctly lower amounts of newly-formed phases over a wide range of temperature.

The reactions of the magnesium compounds to the respective silicate phases are also decisively influenced by the given compound and the chosen mole ratio. As can be seen from Table 2, the lowest reaction degree is obtained for mixtures with magnesium oxide and at low contents of silicic acid.

Table 2 Chemically determined amount of nonconversed MgO after 3 h tempering at 1200 °C for different MgX/SiO_2 mixtures

Mg component	MgO_{free} content, rel. % at a molar $MgO:SiO_2$ ratio of		
	0.5	1.0	1.5
MgO	2.3	36.2	41.1
$MgCO_3$	0.2	22.2	29.5
$MgCl_2$	0.3	8.7	26.9
$MgSO_4$	0.1	11.8	15.1
$Mg(NO_3)_2$	0.1	2.8	12.4

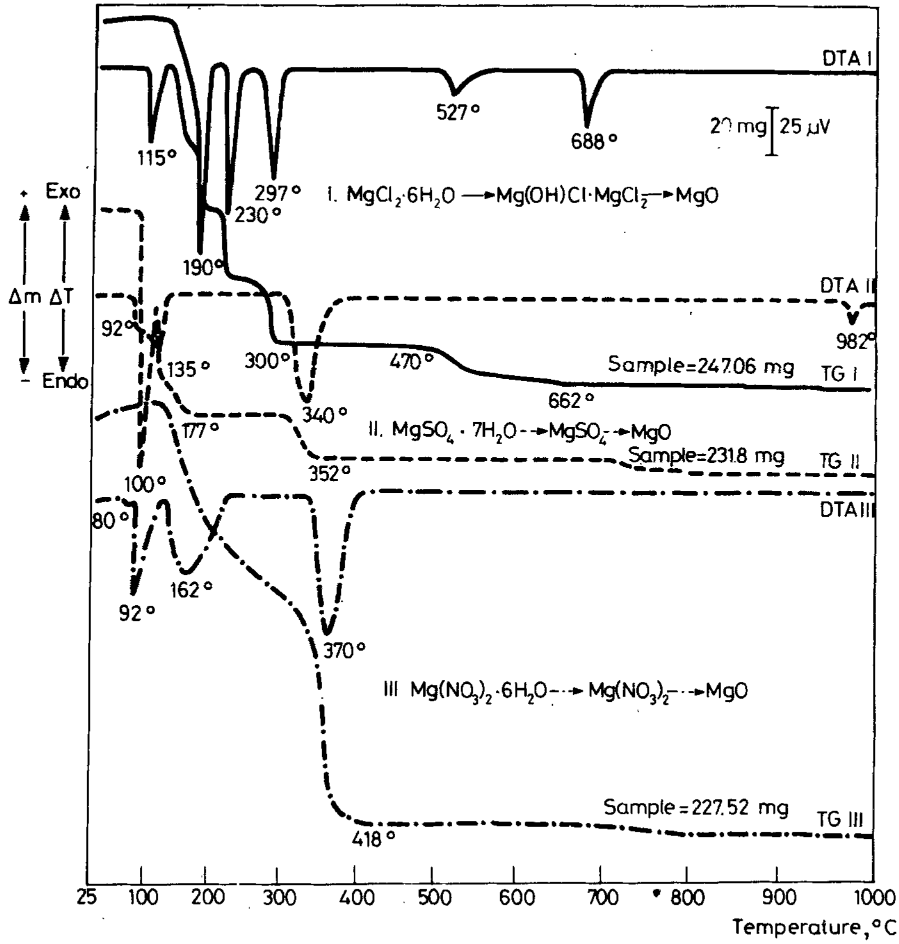

Fig. 2 DTA and TG curves of the thermal decomposition of magnesium salt hydrates at quasi-isothermal heating programme in the labyrinth crucible

In the case of the magnesium salts, reactive intermediates are formed in previous decomposition reactions; through their interaction with quartz sand, these clearly form higher amounts of magnesium silicates.

According to the quasi-isothermal thermoanalytical curves for the magnesium salts $MgCl_2 \cdot 6H_2O$ [3], $MgSO_4 \cdot 7H_2O$ [4] and $Mg(NO_3)_2 \cdot 6H_2O$ [5] presented in Fig. 2 the respective decomposition mechanisms are relatively complicated. As indicated in the literature [3–5], they involve phase transformations, melting processes and the isothermal and nonisothermal splitting of H_2O and acids.

Even at relatively low temperatures, the presence of SiO_2 has an obvious influence on the course of decomposition of magnesium salt hydrates, as clearly seen from the DTG curves in Fig. 3, obtained under dynamic heating.

In view of the specific raw material situation of the G.D.R., for a short time caustic MgO prepared from $MgCl_2$ has been of special interest for industrial use, in addition to magnesite [6, 7]. However, in an evaluation of the chemical phase amounts in the sintered products (Table 2), the distinctly higher reaction conversion of magnesite is striking. The explanation in this case too is that the finely disperse, strongly structurally irregular MgO particles formed by the decarbonization of $MgCO_3$ favour silicate phase formation.

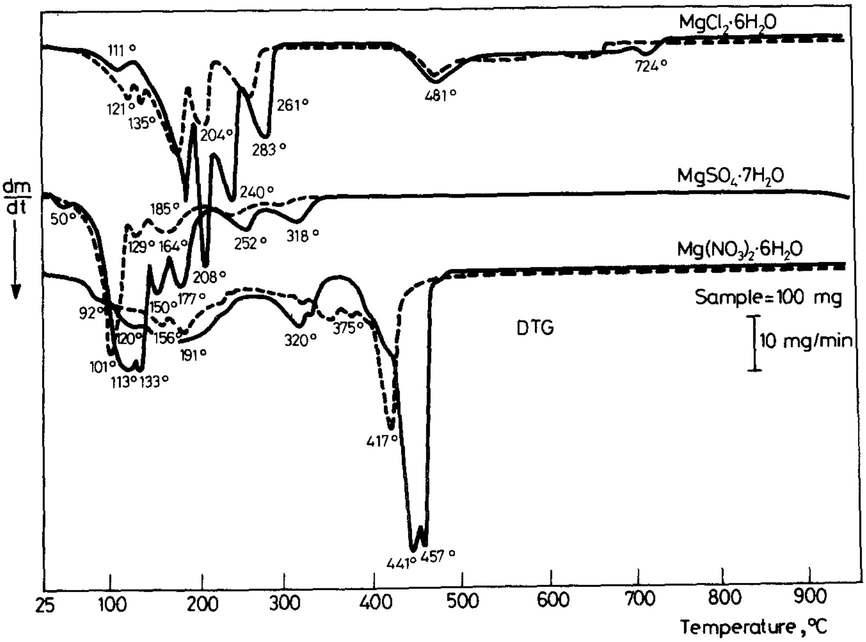

Fig. 3 DTG curves of magnesium salt hydrates and 0.4 molar $MgX-SiO_2$ mixtures obtained at dynamic heating in the open crucible.
—— $MgX \cdot nH_2O$ sample, – – – $MgX \cdot SiO_2$ mixture (0.4 : 1 mol%)

References

1 R. Hayami and T. Ogura, J. Ceram. Assoc. Japan, 75 (1967) 125; 75 (1967) 343.

2 G. Jander and E. Wuhrer, Z. Anorg. Allgem. Chem., 226 (1936) 227.

3 D. Petzold and R. Naumann, J. Thermal Anal., 19 (1980) 25.

4 K. Heide, J. Thermal Anal., 1 (1969) 183.

5 C. Duval, Inorganic Thermogravimetrie Analysis, Elsevier, Amsterdam 1963, p. 218.

6 WP CO4 B/2455988 from 6. 12. 1982.

7 H.- J. Huhn, Silikattechnik (in press).

Zusammenfassung — Über lange Zeit war die Hochtemperatursynthese von Magnesiumsilicaten aus einer Mischung von Magnesit und Quarzsand die Grundlage für die Produktion von Enstatit und die nachfolgende Herstellung von Steatiten in der Keramik-Industrie der DDR. Hier wird gezeigt, dass grundsätzlich auch andere Magnesiumverbindungen mit SiO_2 zu Magnesiumsilicaten umgesetzt werden können. Abhängig von den gewählten mechanischen und thermischen Bedingungen werden unterschiedliche Zwischenprodukte gebildet, die nach dem Brennen Unterschiede in der Phasenzusammensetzung zur Folge haben können. Thermoanalytische Methoden sind gut geeignet, die Reaktivität verschiedener Gemische in fester Phase zu vergleichen.

Резюме — В течении многих лет высокотемпературный синтез силикатов магния из смеси магнезита и кварцевого песка был основным методом получения энстатита и последующего получения стеатитов для керамической промышленности ГДР. В статье показано, что в принципе смеси других соединений магния с двуокисью кремния могщт быть превращены до силиката магния. В зависимости от механических и термических условий, образуются промежуточные продукты с различной реакционной способностью, которые затем после керамического обжига, ответственны за различия в пределах фазового состава. Термоаналитические методы являются пригодными для сопоставления твердотельной реакционной способности различных смесей.