The System $MgO-SiO_2-H_2O$ at Temperatures of 150—350°C under Hydrothermal Conditions

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Received March 26, 1969

The mixtures of magnesium oxide and silicon dioxide were prepared by using various forms of the silicon dioxide. The mixtures with the molar ratio M/S* between 0.3—2.5 were subjected to a hydrothermal process during 6, 12 and 24 hours and at temperatures of 150, 200, 250, 300 and 350°C. The samples thus obtained were investigated by means of X-ray diffraction, DTA, electron microscopy, as well as by chemical analysis. It was found that the first step reaction product was a compound with the molar ratio M/S = 1.5, regardless the molar ratio of the starting mixture. This compound formed a gel in which singular crystals could not be distinguished even by electron microscopy. It was characterized by an expressive exothermic peak of the DTA curve at 850°C and by a weak endothermic deflection in the temperature interval between 500—700°C. With the molar ratio M/S = 1.0, the formation of serpentine and talc was found at 300°C and at higher temperatures. With the molar ratio M/S equal or smaller than 0.75 talc was formed as early as after 24 hours at 300°C or at the temperatures over 300°C, respectively.

Several workers have been engaged in the investigation of the system $MgO-SiO_2-H_2O$. Their studies have been in the first place aimed at the collection of the data concerning the formation of particular phases and their stability under various conditions. Several starting materials have been used. It has been found [1—10] that two compounds exist in this system which correspond to natural minerals, *e.g.* serpentine ($3MgO \cdot 2SiO_2 \cdot 2H_2O$) and talc ($3MgO \cdot 4SiO_2 \cdot H_2O$). There are few data in literature concerning the formation and character of compounds which ensue from the mixtures with various molar ratios M/S at different temperatures during a short duration of hydrothermal process. *Kalousek* [3] followed the rise of singular compounds at different temperatures and in short time intervals. He applied the mixtures with the molar ratio M/S from 0.75 to 2.00.

Regarding the technological hydrothermal process, it has been necessary to verify the results of Kalousek and add the data concerning the mixtures with lower molar ratios M/S.

Experimental

Magnesium oxide was prepared by burning magnesium carbonate (Lachema) at 850°C during two hours. Silicon dioxide (mesh fraction 0.06) was used in the form of β-quartz (99.9% SiO_2), microcrystalline β-quartz ŽK-2 (99.75% SiO_2), silica glass (99.8% SiO_2) and of aerosil (Degussa) (99.3% SiO_2).

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* $MgO = M$, $SiO_2 = S$, $H_2O = H$.

The mixtures with the molar ratios M/S = 0.3, 0.5, 0.8, 1.00, 1.50, 2.00 and 2.50 were prepared by mixing the corresponding amounts of particular components. They were homogenized dry and on adding an excess of hot distilled water. The mixtures, having slurry consistence, were put into an autoclave in silver crucibles and subjected to the hydrothermal process at 150, 200, 250, 300 and 350°C during 6, 12 and 24 hours. Having been collected from the autoclave, the samples were dryed in a drier at 105°C and subjected to a study by using DTA, X-ray diffraction, and electron microscopy. The description of instruments used has been presented in an earlier paper [11]. The portion of SiO_2 which had reacted was determined analytically. After dissolution in 15% HCl, the samples were warmed to 80°C. The consumed portion of SiO_2 was dissolved on a filter in the warm solution (50°C) containing 5% of Na_2CO_3 as well as 5% of NaCl. Then it passed into the filtrate in the form of sodium silicate where it was determined in the usual way. A similar method was previously described by *Steopoe* [12] and used by *Kalousek* [3]. In this study, higher temperatures were employed because the results were not always reproducible when usual temperatures were applied.

Results and Discussion

By means of DTA, it has been found that the samples with the molar ratio M/S = = 0.3, heated at 150°C for 6 till 24 hours, contain a compound which is characterized by an exothermic peak of the DTA curve at 850°C. With samples prepared by 6 till 24 hours' heating at 200 and 250°C, the DTA curves have a broad endothermic deflection in the temperature region from 500 to 700°C, in addition to the exothermic peak. The samples, produced by 6 hours' heating at 300 and 350°C, are characterized by a weak exothermic deflection and those, produced after 24 hours, by an endothermic peak, starting at 800°C. The samples with the molar ratio M/S = 0.5, prepared at temperatures up to 250°C, give DTA curves with an exothermic peak at 850°C. The samples, prepared by 6 hours' heating at 150—250°C, respectively, contain free brucite. The DTA curves of the samples, prepared by 24 hours' heating at 300 and 350°C, are characterized by an endothermic deflection (Fig. 1).

It follows from these results that the reaction runs very slowly at 150°C. But a great difference can be seen in connection with the specific surface of starting materials used. The mixtures prepared from aerosil and microcrystalline quartz react much more quickly than the mixtures prepared from β-quartz and silica glass.

The samples with the molar ratio M/S = 0.8, prepared by 12 hours' heating at 150—250°C, contain brucite. The samples, prepared from aerosil and microcrystalline quartz, contain brucite only after 6 hours when the temperatures of 150—200°C have been applied. The DTA curves of all samples show an exothermic peak at 850°C and a broad endothermic deflection between 500 and 700°C. The samples, containing brucite, give DTA curves with a sharp endothermic peak starting at 400°C. The samples, prepared at 300 or 350°C, respectively, do contain no more free brucite and after 6 or 12 hours are characterized by an exothermic peak at 850°C, whereas the samples, prepared from aerosil and microcrystalline quartz by 24 hours' heating, are characterized by an endothermic peak beginning at 800°C.

The samples with the molar ratio M/S = 1.0, heated at 150—200°C, contain brucite even after 12 hours. Only the samples, prepared from aerosil and microcrystalline quartz, do not contain brucite. The DTA curves of these samples are characterized by an exothermic peak at 850°C.

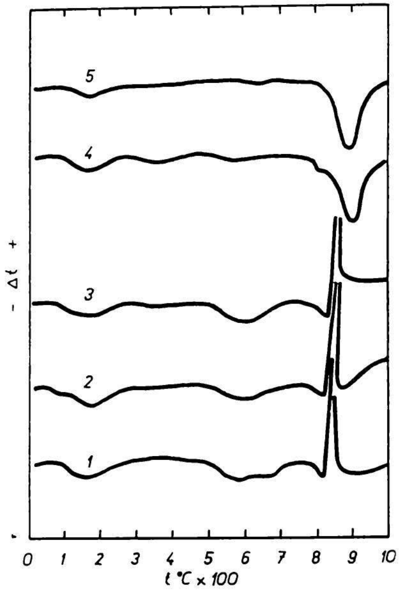

Fig. 1. DTA curves of the samples with the molar ratio M/S = 0.5 after 24 hours' heating at different temperatures.
1. 150°C; *2.* 200°C; *3.* 250°C; *4.* 300°C; *5.* 350°C.

The samples with the molar ratio M/S = 1.5 contain brucite even after 24 hours heating at 150 or 200°C, respectively. Only the sample, prepared from aerosil, does not contain any more brucite after 24 hours' heating at 200°C. No sample contains any more brucite after 24 hours' heating at 250°C. The DTA curves of all samples are characterized by an exothermic peak at 850°C and an endothermic deflection in the temperature interval from 500 to 700°C. In case of a sample, prepared from aerosil and microcrystalline quartz, this deflection gradually gets narrower and more conspicuous with increasing temperature of the hydrothermal process. It also gets similarly narrower in case of other samples, but this phenomenon is less expressive.

The samples with the molar ratio M/S = 2.0 contain brucite invariably at all temperatures used. The content of brucite even increases in case of the samples with the molar ratio M/S = 2.5. In addition to the endothermic brucite peak, the DTA curves of samples are characterized by an exothermic deflection at 850°C which starts at 730°C and double up in case of samples, prepared at 200°C or over this temperature so that a broad twofold exothermic deflection comes into existence. The endothermic deflection between 500—700°C is rather deformed by a large amount of brucite. The DTA curves of samples with the molar ratio between 0.5—2.5, prepared by 24 hours' heating at 200°C, are given in Fig. 2.

It has been found by means of X-ray diffraction that the new crystalline formations, arisen after 6 or 12 hours, respectively, may be characterized only by diffuse lines which can not be attributed to any compound. (The diffraction lines of starting materials that have not reacted are not taken into consideration.) Their intensity increases with increasing temperature, but they remain diffuse even at 350°C. The samples with the molar ratios 0.3, 0.5 and 0.8, heated for 24 hours at 150, 200 and 250°C, also contain only diffuse lines in the range 8—12°, 16—20° and 29—31° Θ,

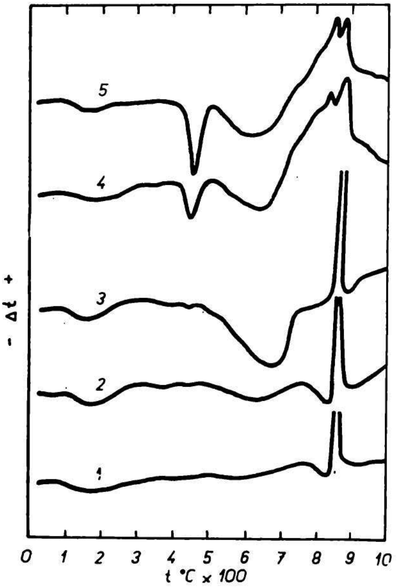

Fig. 2. DTA curves of the samples with the molar ratios M/S = 0.5—2.5 after 24 hours' heating at 200°C.
Molar ratios M/S *1.* 0.5; *2.* 1; *3.* 1.5; *4.* 2; *5.* 2.5.

respectively. Other diffuse lines arise over the range 13.50—14.50° Θ and 4—5° Θ with the samples, prepared at 300°C and their intensity grows in the event the temperature of 350°C has been used. It is obvious from the values d_{hkl} of diffuse lines and bands at 300 and 350°C that it is talc which is formed in these mixtures.

The X-ray diffraction pattern of the samples with the molar ratio M/S = 1.00 is characterized by some diffuse lines and bands like that of samples with a lower molar ratio. The intensity of bands increases as the temperature raises, but none of the components can be determined unambiguously even in the samples prepared at 350°C because the diffraction patterns are more diffuse than in case of the samples with lower molar ratios. Only in the angle range $\Theta = 17-18°$, the diffuse band has two peaks in the samples, prepared at 350°C, which correspond to the values $d_{hkl} = 2.51$ and 2.49 Å, respectively, bellonging to serpentine and talc.

If the samples with the molar ratio M/S = 1.5, corresponding to serpentine, and the temperatures of 150 and 200°C are employed, the X-ray diffraction patterns show two diffuse bands like those of the samples with lower molar ratios. The X-ray diffraction patterns of the samples, prepared at 250°C, contain already the diffraction lines $d_{hkl} = 7.2$ Å, $d_{hkl} = 4.5$ Å, $d_{hkl} = 3.6$ Å and $d_{hkl} = 1.52$ Å, which correspond to serpentine. The intensity of diffraction lines increases with increasing temperature. The diffuse band remains in the angle range from 16 to 20°, but its intensity grows.

All mixtures with the molar ratios M/S = 2.0 and M/S = 2.5 contain free magnesium hydroxide at every temperature. The X-ray diffraction patterns are characterized by diffuse lines and bands and they include the diffraction lines of serpentine when the samples have been prepared at higher temperatures.

The X-ray phase analysis of the samples heated to 1000°C has made evident that enstatite and cristobalite are formed in the samples with the molar ratios M/S from 0.3 to 1.0 containing talc while forsterite and probably enstatite [2] are formed in the samples with the molar ratios M/S equal or larger than 1.0. The enstatite has not been proved unambiguously.

The analysis has shown that the first step of the reaction of magnesium hydroxide with silicon dioxide gives rise to a compound with the molar ratio M/S = 1.5 which goes on reacting with SiO_2 in the starting mixture having the molar ratio M/S < 1.5 under formation of talc. That is why talc is found in these mixtures besides serpentine. In the mixtures with the molar ratio M/S = 0.75, talc is produced by this reaction. The reaction seems to run in steps through several intermediates with the molar ratios M/S from 1.5 to 0.75. It has not, however, been possible to identify these intermediates by the methods used. The results obtained in this study are conform to those of *Kalousek* [3].

It was found by means of electron microscopy that the products of the reaction of magnesium hydroxide and silicon dioxide constitute the crystals which appear in electron microscope as clusters the fibrous character of which can, however, be distinguished only with the samples, prepared at higher temperatures and in a prolonged hydrothermal process. The samples with the molar ratio equal or smaller than 0.75 contain talc in the form of sheet crystals which can be distinguished at 300°C or at higher temperatures, respectively (Fig. 3). In mixtures with the molar ratio M/S = 1.5, prepared at 300°C and at higher temperatures, the particular crystals of serpentine can be distinguished (Fig. 4) and the samples with the molar ratio 2.0 contain a mixture of magnesium hydroxide and serpentine (Fig. 5). The size of serpentine crystals decreases in the samples with the molar ratio M/S = 2.5 what may be due to a large excess of free magnesium hydroxide.

The results thus obtained show that talc is formed as the main component in the mixtures with the molar ratio M/S equal or smaller than 0.75 at 300°C or at the temperatures over 300°C, respectively. It is talc and serpentine that are formed in the mixtures with the molar ratio between 0.75—1.5 at 300°C or at higher temperatures. Serpentine comes into existence in the mixtures with M/S = 1.5 and in case the magnesium oxide content is higher, serpentine and brucite are created. In

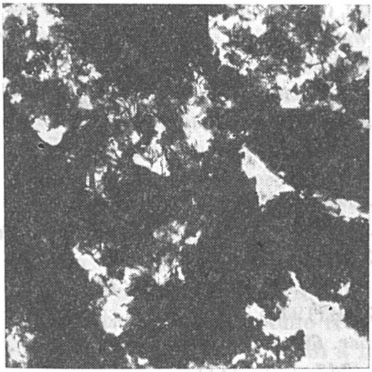

Fig. 3. Electron microscopic picture of a sample with the molar ratio M/S = 0.5 after 24 hours' heating at 350°C; 15,000 fold magnification.

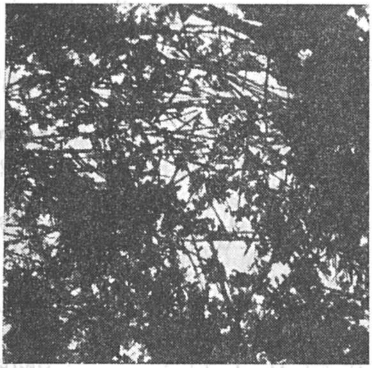

Fig. 4. Electron microscopic picture of a sample with the molar ratio M/S = 1.5 after 24 hours' heating at 350°C; 15,000 fold magnification.

the first step, the reaction product of magnesium hydroxide and silicon dioxide is a compound with the molar ratio M/S = 1.5. Its DTA curve is characterized by a conspicuous exothermic peak at 850°C and by an endothermic deflection in the temperature region from 500 to 700°C. Its X-ray diffraction patterns are characterized by some diffuse lines which can not be attributed to any compound. It reacts with free silicon dioxide when the temperature raises under formation of several intermediates and the final product of these processes is talc which can be identified unambiguously only at 300°C or at the temperatures over 300°C, respectively. Besides serpentine, talc can be identified in the samples with the molar ratio M/S = = 1.0 prepared at 350°C by means of X-ray diffraction.

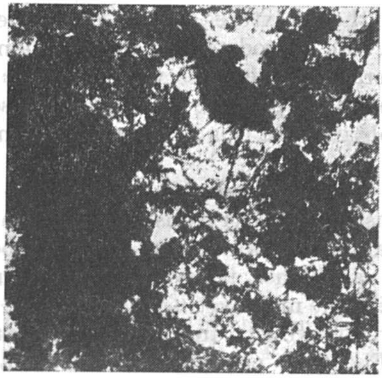

Fig. 5. Electron microscopic picture of a sample with the molar ratio M/S = 2.0 after 24 hours' heating at 350°C; 15,000 fold magnification.

The use of different forms of SiO_2 has had a marked influence neither on the phase composition of samples nor on the rate of the crystal structure formation of particular phases. It has resulted only in a different reaction rate of individual component owing to different specific surfaces.

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Translated by R. Domanský