

Enhanced dehydration and amorphization of $\text{Mg}(\text{OH})_2$ in the presence of ultrafine SiO_2 under mechanochemical conditions

Jiefan Liao and Mamoru Senna

Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223 (Japan)

(Received 3 March 1992)

Abstract

Mechanochemical amorphization and dehydration of fine particulate crystalline $\text{Mg}(\text{OH})_2$ was substantially accelerated by the presence of amorphous SiO_2 . The TG–DTA profile of the mixture consisting of fine powders of $\text{Mg}(\text{OH})_2$ and SiO_2 changed significantly with grinding time whereas only a slight change was observed on grinding pure $\text{Mg}(\text{OH})_2$. Enhanced mechanochemical dehydration of $\text{Mg}(\text{OH})_2$ in the mixture was explained by assuming the following complex processes: intimate mixing, agglutination at the contact points of unlike particles promoted by the higher affinity of silica over magnesia towards hydroxyl groups and initiation of simultaneous solid-state reactions, i.e. addition-reaction between two ingredients and dehydration to form a precursor of magnesium silicate in an amorphous state. The proposed mechanisms were compared with those for the mechanochemical change of talc.

INTRODUCTION

Magnesium silicates can be produced either by decomposition of natural minerals such as talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) or by synthesis. In our previous study on the formation of enstatite from mechanically amorphized talc, a mechanism of inhomogeneous amorphization associated with the layer structure of talc was proposed [1]. A comparison with a material of composition similar to that of talc, but without the layer structure, is desirable in order to examine whether the proposed mechanism for amorphized talc is to be accepted more generally. A fine particulate mixture of $\text{Mg}(\text{OH})_2$ and SiO_2 in a molar ratio of 3:4 seems to be suitable for such a comparative study, because the brucite is located randomly in the mixture instead of being sandwiched by hexagonal silica layers as in the case of talc.

Correspondence to: M. Senna, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223, Japan.

Many examples of mechanochemical reactions are now known for the complex reactions initiated directly by applied mechanical energy [2, 3]. Although the mechanochemical changes of pure $\text{Mg}(\text{OH})_2$ [4] or SiO_2 [5] have been previously studied, the mechanochemical reaction of a mixture of $\text{Mg}(\text{OH})_2$ and SiO_2 remains unexplored.

The grinding of a mixture (hereafter called mixed-grinding) is becoming a new technique of synthesis [6–10]. One example is mechanical alloying which is currently attracting ever-increasing attention [6]. Mechanochemical reactions during mixed-grinding of inorganic compounds with different structures are obviously more complicated than those of a pure metallic system. It was found that the mixed-grinding of an $\text{NiO}-\text{MoO}_3$ mixture in air accelerated the solid-state reaction on subsequent heating at 600°C , presumably because of precursory products formed at the contact points between the unlike reactant particles during mixed-grinding [11]. A similar mechanism was hypothesized for the formation of the superconductive material CuBi_2O_4 by grinding a mixture of Bi_2O_3 and CuO [9]. ZnFe_2O_4 was synthesized directly by grinding a $\text{ZnCO}_3-\text{Fe}_2\text{O}_3$ mixture [12]. However, the experimental and theoretical studies published on these complex reactions are insufficient [13]. The mechanochemical reaction of a mixture of solids during grinding is often beyond the scope of conventional thermodynamic equilibria [14], mainly because of the existence of short-lived highly activated local sites.

The present study was carried out in order to understand the solid-state reaction, initiated by mechanical activation, between $\text{Mg}(\text{OH})_2$ and SiO_2 powders. The mechanochemical effects on the thermal behaviour of these mixtures on subsequent heating, which produce magnesium silicates, were also studied. Comparison was made with our previous results on talc [1].

EXPERIMENTAL

Crystalline $\text{Mg}(\text{OH})_2$ was prepared by ionic precipitation by adding 1 M aqueous ammonia solution to 1 M aqueous magnesium chloride solution at 25°C . The obtained precipitate was washed repeatedly with deionized water until no Cl^- was detected by 0.1 M AgNO_3 , and then dried at 50°C until the weight became constant. The amorphous SiO_2 powder (Aerosil 200, Japan Aerosil) was used without any pretreatment. The $\text{Mg}(\text{OH})_2$ and a mixture of $\text{Mg}(\text{OH})_2$ and SiO_2 in the molar ratio 3:4 were ground using a laboratory-sized vibration mill (Glen-Creston). Details of the equipment are given elsewhere [1]. One gram of sample was ground batch-wise in air with varying grinding times. The ground $\text{Mg}(\text{OH})_2$ samples are denoted M- t , where t indicates the grinding time in hours. Similarly, the mixed-ground $\text{Mg}(\text{OH})_2-\text{SiO}_2$ samples are denoted MS- t .

The ground samples were characterized simultaneously by differential thermal analysis (DTA) and thermogravimetry (TG), using a thermo-

analyser (Thermoflex, Rigaku). The measurement was made in a stream of N_2 with a flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$, using $\alpha\text{-Al}_2\text{O}_3$ as the reference, and raising the temperature linearly at 10 K min^{-1} . BaCO_3 was used as reference standard for the determination of the enthalpy change in the DTA analysis. The structure of the samples was characterized by X-ray diffractometry (XRD, Rigaku, CN2013), using $\text{Cu K}\alpha$ radiation and a graphite monochromator. The infrared spectra were recorded by means of an FT-IR spectrometer (BIO-RAD, FTS-65), using a KBr disc method. The particulate morphology was monitored by scanning electron microscopy (JEOL, JSM 5200).

RESULTS AND DISCUSSION

Amorphization during separated- and mixed-grinding

XRD patterns for the ground $\text{Mg}(\text{OH})_2$ are shown in Fig. 1. Most of the decrease in crystallinity took place during the first half-hour. The structure of $\text{Mg}(\text{OH})_2$ was still evident after grinding for 48 h (sample M-48). A small peak at around $2\theta = 44.5^\circ$ is attributed to the presence of iron impurity due to abrasion of the grinding ball and vessel. In the case of mixed-grinding, in contrast, amorphization occurred rapidly at the early stage of grinding, as shown in Fig. 2. No diffraction peak except that of Fe was observed after grinding the mixture for 2 h.

By comparing Fig. 1 with Fig. 2, it can be seen that the amorphization of $\text{Mg}(\text{OH})_2$ takes place much easier by mixed-grinding than by grinding

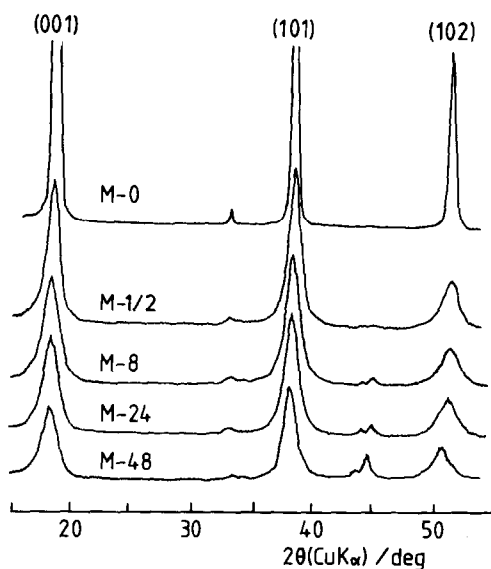


Fig. 1. XRD patterns of the initial $\text{Mg}(\text{OH})_2$ and the ground samples, M- t , where t indicates the grinding time in hours.

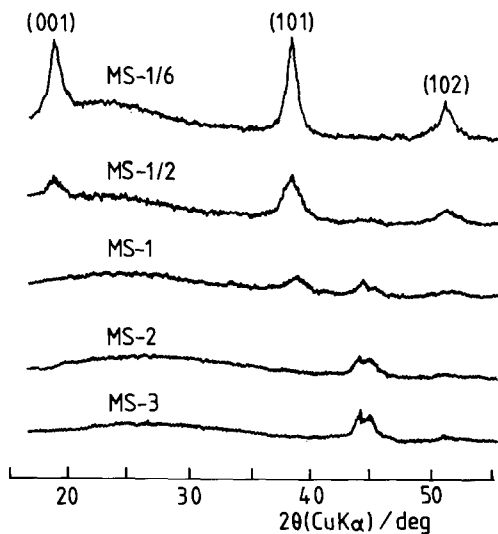


Fig. 2. XRD patterns of the $\text{Mg}(\text{OH})_2\text{-SiO}_2$ mixtures, MS- t , where t indicates the grinding time in hours.

pure $\text{Mg}(\text{OH})_2$. Mechanical activation of a solid is usually used to increase its reactivity, because a part of the supplied mechanical energy is stored as excess enthalpy. About 70–98% of the net energy change may be attributed to amorphization [15]. It is found that the excess enthalpy ΔH^* , due to mechanical activation depends on the method of mechanical pre-treatment [16]. Because all the conditions, except grinding time, of the mechanical treatment were unchanged from the previous study [1], the difference in the rate of amorphization between $\text{Mg}(\text{OH})_2$ and talc should be attributed to the different nature of these two materials. By comparison with the previous study [1], it is found that the rate of amorphization of an $\text{Mg}(\text{OH})_2\text{-SiO}_2$ mixture is similar to that of talc, i.e. both were amorphized within two hours, in spite of their different original structures. The presence of SiO_2 is thus most likely to be responsible for the fast amorphization in the mixed-grinding. In other words, mechano-chemical change of $\text{Mg}(\text{OH})_2$ is strongly influenced by the presence of the second component SiO_2 .

Results of FTIR analysis

As shown in Fig. 3, the intense absorption band at 3650 cm^{-1} , due to the vibration of proton against oxygen in the $\text{Mg}(\text{OH})_2$ structure [17], was present even after grinding $\text{Mg}(\text{OH})_2$ for 48 h. In contrast, this adsorption band decreased rapidly after mixed-grinding, and vanished after grinding for 2 h, as shown in Fig. 4. Similarly, the absorption band at 790 cm^{-1} , due to the Si–O–Si symmetric stretching vibration [18], was observed on the

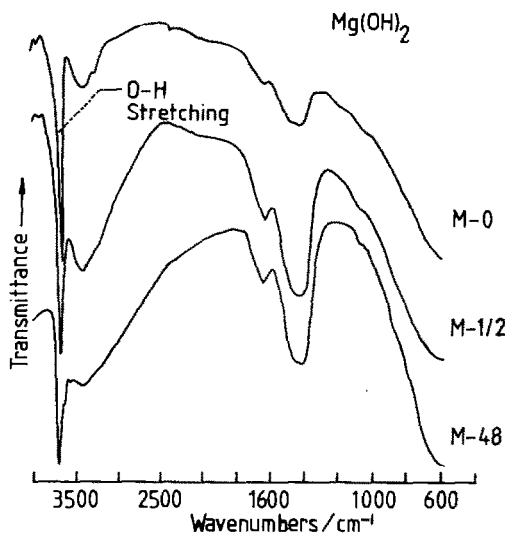


Fig. 3. FTIR spectra of the initial Mg(OH)_2 and the ground samples.

spectrum of MS-1/6, but disappeared on MS-2. The adsorption bands at around 3400 and 1630 cm^{-1} are attributed to the silanol group and to adsorbed water [18] on the surface of the particles respectively. The interactions between the adsorbed species should be responsible for the observed broadening around 3400 cm^{-1} during mixed-grinding. Grinding

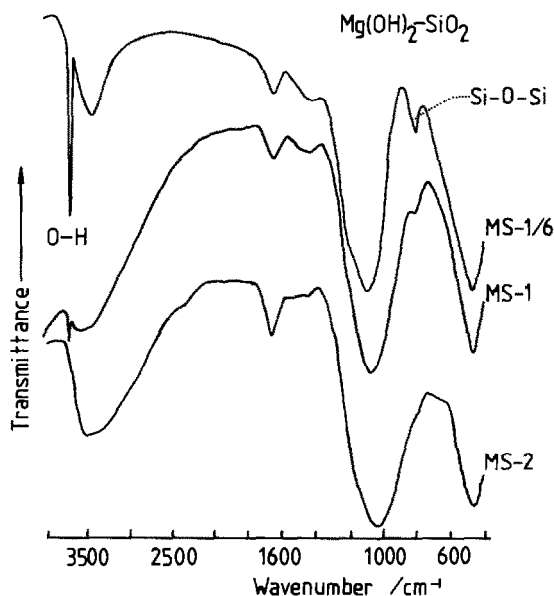


Fig. 4. FTIR spectra of the $\text{Mg(OH)}_2\text{-SiO}_2$ mixtures ground for different times.

of pure SiO_2 was also performed: all the absorption bands from intact SiO_2 remained after grinding for 2 h.

These results, together with those of XRD and TG–DTA, suggest that the $\text{Mg}(\text{OH})_2$ – SiO_2 mixture was a simple physical mixture of $\text{Mg}(\text{OH})_2$ and SiO_2 particles only at the very early stage of grinding, this was followed by a rapid change into a chemically interacted complex.

Dehydration and crystallization

The thermal behaviour of $\text{Mg}(\text{OH})_2$ samples ground for up to 48 h showed no significant change, as shown in Fig. 5. This suggests that the dehydration of $\text{Mg}(\text{OH})_2$ is very slow compared with that of talc [1]. In their experimental study on the mechanical activation of $\text{Mg}(\text{OH})_2$, Gregg and Saenz [19] found that the dehydration temperature of $\text{Mg}(\text{OH})_2$ was not appreciably altered by grinding for less than 350 h, but that it was slightly lowered above 350 h with the structural distortion. Arai et al. [20] found that mechanochemical dehydration of $\text{Mg}(\text{OH})_2$ took place when $\text{Mg}(\text{OH})_2$ was ground in a vacuum (1×10^{-2} Torr or 1.3 Pa) using an automatic mortar made of super-hard alloy. The present results again confirms that pure $\text{Mg}(\text{OH})_2$ is difficult to dehydrate, at least when mechanochemical treatment is carried out in air.

In contrast, the dehydration of pure ground $\text{Mg}(\text{OH})_2$, by heating at temperatures from 300 to 500°C , was not observed on mixed-ground

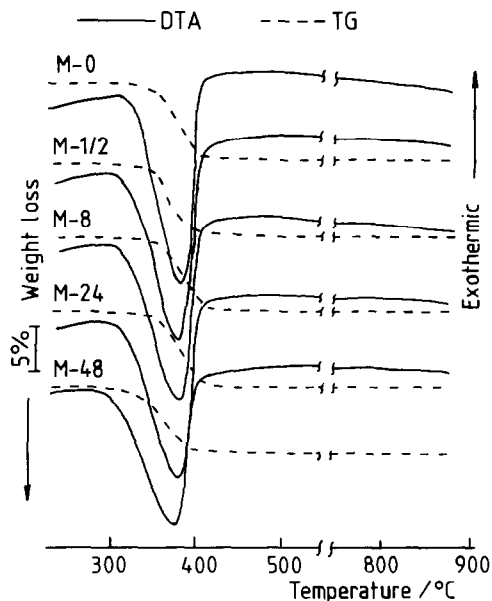


Fig. 5. TG–DTA profiles of the initial $\text{Mg}(\text{OH})_2$ and the ground samples.

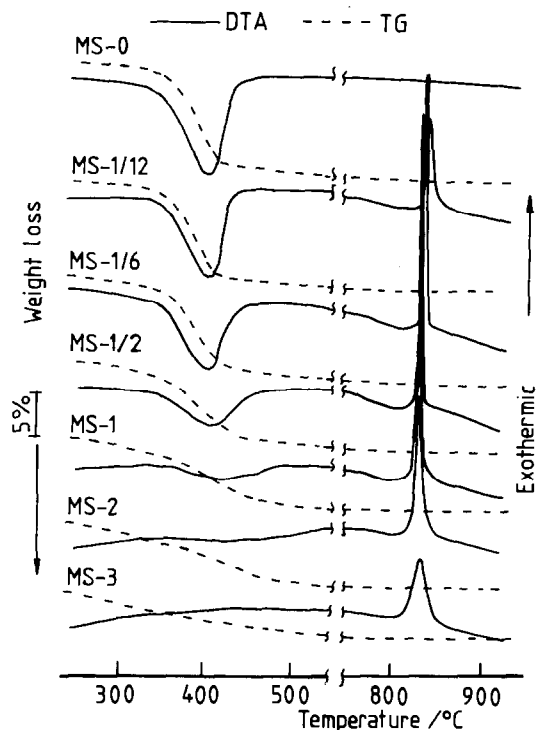


Fig. 6. TG-DTA profiles of the $\text{Mg}(\text{OH})_2\text{-SiO}_2$ mixtures with and without grinding.

samples MS-1 and MS-2, as shown in Fig. 6. Instead, an exothermic peak appeared at around 825°C for the mixed-ground samples. The change in the enthalpy at this temperature ΔH varied with grinding time in a manner shown in Fig. 7. The change in the TG-DTA profiles of the mixed-ground samples with varying grinding time is quite similar to that of talc, except for the maximum in the heat evolved $-\Delta H$ at 0.5 h grinding.

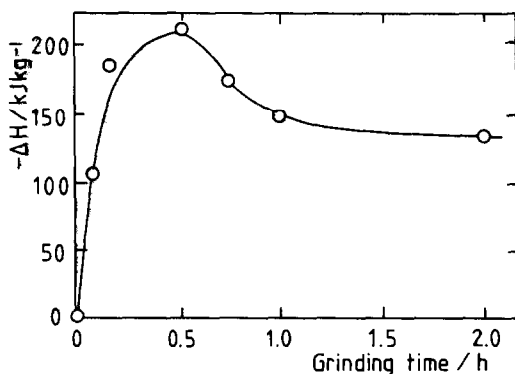


Fig. 7. The relationship between the change in the enthalpy $-\Delta H$ at the peak temperature and the mixed-grinding time.

The decrease in $-\Delta H$ was observed for the samples without an intensive weight loss on subsequent heating, i.e. for the samples with substantial mechanochemical dehydration. This might be attributed to the easier nucleation of the magnesium silicate crystals.

By comparing the results of XRD and TG-DTA, some correlation can be found between them. The X-ray diffraction peaks of $\text{Mg}(\text{OH})_2$ almost disappeared on the pattern of MS-1, while the endothermic peak also disappeared on the DTA profile of the same sample. The intensive weight loss in the temperature range from 350 to 400°C for MS samples with grinding times less than 1 h should be due to the dehydration or detachment of $-\text{OH}$ groups. Therefore, the disappearance of the characteristic dehydration of $\text{Mg}(\text{OH})_2$ on heating the mixed-ground samples with longer grinding time suggests that mechanochemical dehydration has taken place during grinding.

Ground samples were heated up to temperatures of 550, 800 and 880°C in a stream of N_2 ($200 \text{ cm}^3 \text{ min}^{-1}$) at the rate of 10 K min^{-1} . This experiment was made in order to examine whether heating of mixed-ground samples results in the same products as were obtained from mechanically amorphized talc [1]. The results of XRD analysis of the samples heated to 550 and 800°C, i.e. before the exothermic peak of Fig. 6, are shown in Fig. 8. For the samples heated up to 550°C, the diffraction peaks of MgO were observed on the patterns of the samples with very short grinding time, i.e. MS-1/6. The MgO obviously resulted from the dehydration of $\text{Mg}(\text{OH})_2$. This suggests that some of the free $\text{Mg}(\text{OH})_2$, which showed the same thermal behaviour as pure $\text{Mg}(\text{OH})_2$, was still present in the early stage of mixed-grinding. However, for the samples with longer mixed-grinding, such as MS-2, their XRD patterns showed no change after being heated up to 550°C. This indicates that no free $\text{Mg}(\text{OH})_2$ remained after 2 h of mixed-grinding. These results are in agreement with those obtained from TG-DTA and FTIR. After the ground samples were heated up to 800°C, the diffraction peak of MgO still

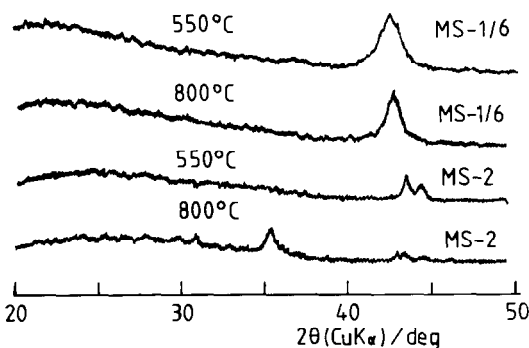


Fig. 8. XRD patterns of the mixed-ground samples heated to 550 and 800°C, respectively.

remained on the pattern of MS-1/6. For the sample MS-2, a small peak appeared at $2\theta = 35.5^\circ$ which should be due to the diffraction of the formed magnesium silicate with low crystallinity. It is thus revealed from Fig. 8 that the addition reaction took place on heating the mixture with longer mixed-grinding time, at temperatures lower than the conventional magnesium silicate formation. The Fe impurity might have participated in the formation of magnesium silicates during heating, and this could be the reason for the disappearance of its diffraction peaks after heating the sample MS-2 up to 800°C . This does not alter the conclusion, however, that the amorphization and dehydration of $\text{Mg}(\text{OH})_2$ are promoted by the presence of SiO_2 .

After heating up to 880°C , the diffraction peaks of MgO were only observed for the mixture that had not been ground, together with a trace of Mg_2SiO_4 (forsterite) (see Fig. 9). For the mixed-ground samples, diffraction peaks of forsterite and MgSiO_3 (enstatite) were recognized, but no peaks from MgO. It is to be noted that only the diffraction peaks of MgSiO_3 were observed for the intensively ground sample, i.e. MS-3. This was also the case for mechanically amorphized talc [1]. The phase of the products obtained by heating the $\text{Mg}(\text{OH})_2$ - SiO_2 mixture thus depends on the grinding time. The amount of forsterite decreased while that of

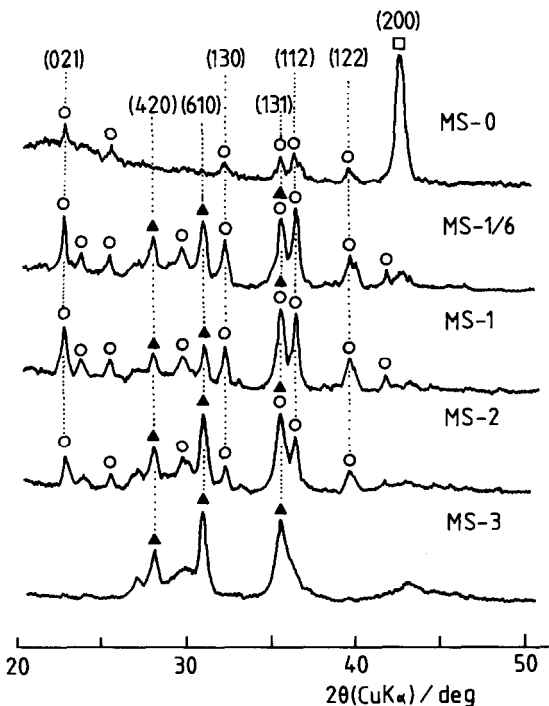


Fig. 9. XRD patterns of the mixed-ground samples heated to 880°C . Key: \square , MgO; \circ , Mg_2SiO_4 ; \blacktriangle , MgSiO_3 .

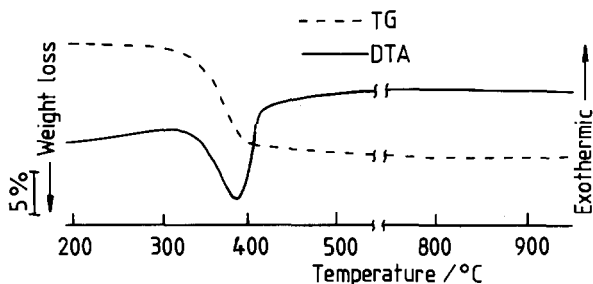


Fig. 10. TG-DTA profile of the mixture of $\text{Mg}(\text{OH})_2$ and SiO_2 , previously ground separately for 2 hours.

enstatite increased with increasing grinding time, gradually approaching the behaviour of talc [1]. When heating talc, no forsterite was found, as shown in our previous study, irrespective of whether or not it had been mechanically activated [1].

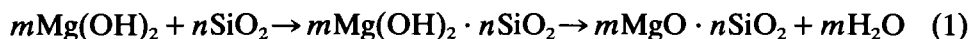
Pure $\text{Mg}(\text{OH})_2$ and pure SiO_2 were ground separately for 2 h and then mixed carefully in a 3:4 molar ratio in acetone, using an agate mortar in order not to give additional significant mechanochemical effects. After the acetone had been fully vaporized in air, the separately ground mixture was then subjected to TG-DTA analysis. As shown in Fig. 10, the TG-DTA profile showed little difference from those of the $\text{Mg}(\text{OH})_2$ - SiO_2 mixture without grinding (compare with Fig. 6, MS-0), but showed considerable differences from those of the mixed-ground samples, in spite of using the same grinding conditions.

Mechanism of the mechanochemical reaction

In a system such as $\text{Mg}(\text{OH})_2 + \text{SiO}_2$, where one of the reaction partners may be dehydrated, it is important to consider the role of H_2O or $-\text{OH}$. Longo and Voight [21] synthesized dolomite by mixed-grinding of the corresponding chlorides or sulphates with sodium carbonate containing crystal water. They suggested that the rapid reaction was attributed to the local high solubility of the components in thin films of water at the grinding surface, because the system they studied contained hydroxyl groups in the form of H_2O as crystal water. The role of water as a solvent in a system similar to that under investigation here was also discussed by Juhász and Pátkai-Horváth [22]. However, their mechanism does not seem to be fully applicable in the present system which contains hydroxyl in the form of $-\text{OH}$ instead of H_2O . The idea that solid-state reactions in mixed-grinding proceeds in a thin film of water adsorbed from air was rejected by Boldyrev [23]. Avvakumov and Kosova [24] found that in the course of mechanochemical synthesis of calcium silicate, the interaction rate of hydroxides was considerably higher than that of oxides, but they gave no explanation for this.

As discussed above, amorphization and dehydration of $\text{Mg}(\text{OH})_2$ were promoted significantly in the presence of amorphous SiO_2 during mixed-grinding. This should not be attributed to the dissolution of SiO_2 and $\text{Mg}(\text{OH})_2$ into the water already contained in the sample or possibly adsorbed from air. It seems more reasonable to interpret the promotion of dehydration and amorphization of $\text{Mg}(\text{OH})_2$ as a result of the incipient solid-state reaction between $\text{Mg}(\text{OH})_2$ and SiO_2 .

Arai et al. [25] investigated the mixed-grinding of $\text{Al}(\text{OH})_3$ and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. They found a mechanochemical dehydration and a considerable increase in the solid acidity on the surface, caused by ion exchange between Al^{3+} and Si^{4+} at the contact point of the dissimilar particles. In the present experiment, some of the $\text{Mg}(\text{OH})_2$ and SiO_2 particles may be agglutinated as a result of atomic or ionic exchange at the contact points. This is to be anticipated, because mechanically activated silica may have a very high affinity towards the hydroxyl group of $\text{Mg}(\text{OH})_2$. This phenomenon is expressed as the solid-state reaction



where the ratio of $m:n$ is not necessarily equal to 3:4. As a result of this reaction, a precursor of magnesium silicate, $m\text{MgO} \cdot n\text{SiO}_2$, is formed. According to the bond energy data [26], the relationship of the bond strengths can be expressed as



It is then reasonable to assume that the $-\text{OH}$ group bound to Mg^{2+} would transfer to Si^{4+} and subsequently produce one water molecule from two $-\text{OH}$ groups. This process results in an O^{2-} ion with a high mobility, as in the case of talc [1]. Such O^{2-} ions can then immediately participate in the rearrangement of the linkages of the SiO_4 tetrahedra, which leads to the formation of a new chain structure of forsterite.

The main points of the present model are, (1) the dehydration and formation of the precursor $m\text{MgO} \cdot n\text{SiO}_2$ take place at the same time at the contact points between unlike particles, and (2) the dehydration and formation of the precursor of magnesium silicates occur simultaneously in different local spots in a grinding vessel when we observe the whole system. With this kind of simultaneous complex process, it seems possible to explain the observed fast amorphization, dehydration and mechanochemical addition-reaction occurring during mixed-grinding.

Mechanism of the formation of forsterite and enstatite

The mechanisms of the formation of forsterite and enstatite are similar to those of the conventional thermal process, but occurring at an elevated rate as a result of the mechanical activation. For the $\text{Mg}(\text{OH})_2$ - SiO_2

mixture without grinding, there is no chemical interaction between $\text{Mg}(\text{OH})_2$ and SiO_2 particles. When it is heated up to 300°C , the thermal dehydration of $\text{Mg}(\text{OH})_2$ takes place, being complete at about 500°C . When the mixture is heated up to temperatures higher than 800°C , the thermal reaction between MgO and SiO_2 can take place. The solid-state reaction produces forsterite much faster than enstatite, irrespective of the molar ratio of the components [27]. Formation of forsterite may take place rapidly at temperatures above 1000°C . It is also expected that the reaction temperature decreases by mechanical activation of the solids [22]. Taking MS-1/2 or MS-1 as an example, some of the $\text{Mg}(\text{OH})_2$ and SiO_2 is involved in the mechanochemical reaction and forms an amorphous precursor of magnesium silicate. Thus, when MS-1/2 or MS-1 is calcined, solid-state reactions between these differently activated solids take place. The reactions include the dehydration of the remaining $\text{Mg}(\text{OH})_2$ and the formation of magnesium silicates from the amorphous precursor. The product Mg_2SiO_4 from the reaction of MgO and SiO_2 is subsequently converted to enstatite by a reaction with the free SiO_2 residue [28].

Effects of particle size

It must be mentioned that particle size may influence the mechanochemical dehydration of hydroxyl compounds. The decomposition temperatures of some solids decrease with decreasing particle size and increasing surface area [29].

Scanning electron microscopy (SEM) revealed that the initial SiO_2 particles formed spherical aggregates approximately $10\ \mu\text{m}$ in size, whereas those of $\text{Mg}(\text{OH})_2$ aggregated in an irregular shape ranging from 2 to $20\ \mu\text{m}$ in size. During the very early stages of mixed-grinding, physical mixing mainly takes place with a simultaneous deagglomeration of $\text{Mg}(\text{OH})_2$ and SiO_2 . Fine particles of $\text{Mg}(\text{OH})_2$ and SiO_2 then brought into more intimate contact with each other, and some new aggregates containing two different fine particulate species are formed, as described by Avvakumov [13]. This was also found for an NiO-MoO_3 mixture [11]. The aggregates of the mixed-ground samples (MS-1, MS-2) are also irregular, ranging in size from 2 to $10\ \mu\text{m}$, while spherical aggregates like those of pure SiO_2 were no longer observed.

The change in the crystallite size D of $\text{Mg}(\text{OH})_2$ during grinding was estimated from the integral peak width of the XRD patterns, using the Scherrer equation. $D(101)$, $D(001)$ and $D(102)$ decreased from 20, 16 and 13 nm, respectively, to 6–8 nm within one hour and then remained constant afterwards. Because the thermal behaviour of pure $\text{Mg}(\text{OH})_2$ showed little change with subsequent grinding time, it is concluded that the change in the crystallite size does not influence the mechanochemical dehydration of pure $\text{Mg}(\text{OH})_2$. Similarly, the effect of the change in the

crystallite size on the mechanochemical dehydration in mixed-grinding is not important.

CONCLUSION

When crystalline $\text{Mg}(\text{OH})_2$ and amorphous SiO_2 powders (in 3:4 molar ratio) are ground together, rapid amorphization and mechanochemical dehydration of $\text{Mg}(\text{OH})_2$ take place. The precursor of magnesium silicates is formed at the same time as a result of a direct solid-state reaction. The presence of SiO_2 during grinding facilitates the dehydration and amorphization of $\text{Mg}(\text{OH})_2$.

ACKNOWLEDGMENTS

Acknowledgment is made to the Toka Education and Culture Exchange Foundation, Tokyo, for a scholarship to J.L. Dr. T. Isobe is thanked for valuable discussion.

REFERENCES

- 1 J. Liao and M. Senna, *Thermochim. Acta*, 197 (1992) 295.
- 2 V.V. Boldyrev, in C.N.R. Rao (Ed.), *Advances in Solid State Chemistry*, Indian National Science Academy, New Delhi 1986, p. 400.
- 3 G. Heinicke, *Tribochemistry*, Akademie Verlag, Berlin, 1984, p. 13.
- 4 S. Inoue and M. Senna, *React. Solids*, 5 (1988) 155.
- 5 U. Steinike, U. Kretzschmar, I. Ebert and H-P. Hennig, *React. Solids*, 4 (1987) 1.
- 6 E.Y. Ivanov, i.G. Konstanchuk, B.D. Bokhonov and V.V. Boldyrev, *React. Solids*, 7 (1989) 167.
- 7 R. Rogue-Malherbe, J. Onate-Martinez and J. Fernandez-Bertran, *Solid State Ionics*, 46 (199) 193.
- 8 T. Isobe, S. Komatsubra and M. Senna, *Nippon Kagaku Kaishi*, (1991) 1361.
- 9 K. Amita and G. Hashizume, *Nippon Kagaku Kaishi*, (1991) 1442.
- 10 V.V. Zyrjanov, in E.G. Avvakumov (Ed.), *Mechanochemical Synthesis in Inorganic Chemistry*, Nauka, Novosibirsk, 1991, p. 102 (in Russian).
- 11 M. Senna and H. Kuno, *Jpn. Soc. Powder Powder Metall.*, 30 (1983) 225.
- 12 N. Lefelshtel, S. Nadiv, I.J. Lin and Y. Zimmels, *Powder Technol.*, 20 (1978) 211.
- 13 E.G. Avvakumov, *Mechanical Methods of Activations of Chemical Process*, Nauka, Novosibirsk, 1986, p. 250 (in Russian).
- 14 Ref. 3, p. 97.
- 15 K. Tkáčová, *Mechanical Activation of Minerals*, Elsevier, Amsterdam, 1989, p. 32.
- 16 K. Miyasaka and M. Senna, *Thermochim. Acta*, 83 (1985) 225.
- 17 V. Stuvičan and R. Roy, *Z. Kristallogr.*, 115 (1961) 200.
- 18 H. Yoshino, K. Kamiya and H. Nasu, *J. Non-Cryst. Solids*, 126 (1990) 68.
- 19 S.J. Gregg and J.P. Saenz, *J. Appl. Chem.*, 16 (1966) 300.
- 20 Y. Arai, T. Yasue and H. Miyake, *Nippon Kagaku Kaishi*, (1972) 547.
- 21 J.M. Longo and K.C. Voight, *Solid State Ionics*, 32/33 (1989) 409.
- 22 A.Z. Juhász and M. Pátkai-Horváth, *Hung. J. Ind. Chem.*, 16 (1988) 439.
- 23 V.V. Boldyrev, in G. Jimbo (Ed.), *Proc. Second Japan–Soviet Symp. Mechanochemistry*, Soc. Powd. Tech. Jpn., Kyoto, 1988, p. 1.

- 24 E.G. Avvakumov and N.V. Kosova, *Sib. Chem. J.*, (5) (1991) 62.
- 25 Y. Arai, T. Yasue, I. Yamaguchi and T. Sugino, *Nippon Kagaku Kaishi*, (1974) 49.
- 26 J.A. Kerr, in D.R. Lide (Ed.), *Handbook of Chemistry and Physics*, 71st edn., CRC Press, Boston, 1990, pp. 9–86.
- 27 G.W. Brindley and R. Hayami, *Philos. Mag.*, 12 (1965) 505.
- 28 R. Hayami, *J. Ceram. Assoc. Jpn.*, 75 (1967) 343.
- 29 A. Nastro, F. Crea and G. Giordano, *J. Therm. Anal.*, 36 (1990) 2223.