CaCl₂ Addition Effect and Melt Formation in Low-Temperature Decomposition of Chrysotile with CaCO₃

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Chrysotile の低温分解における CaCl₂ 添加効果と融体形成

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Mixtures of chrysotile (Mg₃Si₂O₅(OH)₄) and CaCO₃ were burned at temperatures ranging from 500°C to 1000°C; the decomposition temperature of chrysotile was lowered by adding CaCl₂. Thermal analysis and succeeding SEM observation confirmed the formation of melts, which was supposed to be responsible for the effect of the added CaCl₂. The melts were detected even when the added CaCl₂ was as little as 1–5 mass% of the CaCO₃; the quantity of the CaCl₂ was smaller than that predicted from the phase diagram. Thermodynamic calculations of chemical equilibrium showed that forsterite (Mg₂SiO₄), which was a thermal decomposition product of chrysotile and had a fibrous shape, destructed at about 500°C. In the common decomposition methods to convert asbestos–cement composites to oxides of Ca–Si system, the decomposition reaction occurs via a solid-solid reaction and reacts slowly. So to increase the reaction rate, a reaction temperature above 1000°C is required. The present study has experimentally evidenced that the formation of melts enlarges the reaction interface between the chrysotile and the CaCO₃ so that the decomposition reaction can proceed even at lower temperatures.

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1. Introduction

A number of methods for decomposition of asbestos have been reported and patented, but only a few reports comprise low-temperature decomposition at temperatures as low as 700–800°C.^{1)–5)} We reported that chrysotile started degradation at 500°C and was pulverized at 700°C when heated together with residue obtained by neutralizing the thermal-decomposition gas of flon with lime slurry (hereafter, flon-decomposition products).²⁾ We also reported that: (1) in this decomposition process, the constituent elements Mg and Si of chrysotile reacted with flon-decomposition products and separated from each other into MgO and CaSiO₃-group compounds; (2) CaCl₂ involved in flon-decomposition products in the amount of about 1 mass% as a contaminant was effective for lowering the decomposition temperature.^{2),3)} Thermal treatment was also carried out on asbestos materials simulated by mixing asbestos with cement, which was used as a CaO source, and on actual sprayed-on asbestos waste that was impregnated in advance with solution of salts such as CaCl₂; in this study, asbestos was found to be decomposed.^{4),5)}

For decomposing similar building materials of asbestos-containing cement, the methods previously reported and patented required the elevation of temperature above 1000°C. In contrast, our method described above decomposed even actual sprayed-on asbestos at a lower temperature of 800°C. This difference can be interpreted as follows. In the former methods, a solid–solid reaction occurs between asbestos and cement components only at points of contact so that the reaction rate is low. A reaction temperature above 1000°C is, therefore, required to increase the reaction rate. On the other hand, the reaction rate of the systems containing a small quan-

tity of CaCl₂ is thought to be increased by the formation of melts that extend the reaction interface even at a temperature as low as 700°C, because the CaCl₂–CaO phase diagram shows a melt at 750°C and a position of 6.5 mol% CaO and the CaCl₂–CaCO₃–CaO phase diagram involves a melt at 750°C in a wide composition range and a ternary eutectic point at 615°C.^{4),6)–8)} The system involving flon-decomposition products showed a tendency for the product to be fused.³⁾ In the systems to which salts such as CaCl₂ were added, a slight sintering was observed for the decomposition products, but evidence for the presence of a melt was not found because the quantity of added CaCl₂ was small.^{4),5)}

In the present study, therefore, mixtures of chrysotile and calcium carbonate were treated by heating at different temperatures, and the power X-ray diffraction patterns of the products were compared with those of the burning products of the samples to which CuCl₂ in 5 mass% of CaCO₃ was added. The formation of melts in chrysotile + calcium carbonate + CaCl₂ systems was investigated by thermal analysis. Melting and adhesion were inspected for the decomposition products with a scanning electron microscope (SEM). In addition, thermodynamic analysis of these reactions was carried out by the use of thermodynamics data base MALT^{9)–12)} in order to explain the reason why decomposition starts at 600°C in our reaction systems while the reaction temperatures of the majority of previously reported methods exceed 1000°C. The results of these studies are reported in this paper.

Table 1. List of Samples Prepared

Sample number	(mol ratio)			
	Chrysotile	Forsterite ^{*1}	CaCO ₃	CaCl ₂
A	0.5		3	
B	0.5		3	5 mass%
C				1
D			1	
E			1	1 mass%
F			1	5 mass%
G		1	2	
H		1	2	5 mass%

*1 : Forsterite used was obtained by burning chrysotile at 800°C for 2 h. Since chrysotile was decomposed to forsterite, amorphous SiO₂, 1 mol of forsterite in Table 1 contained 1/3 mol of amorphous SiO₂ each.

2. Experimental

2.1 Thermal decomposition of chrysotile with calcium carbonate

The mixing mole ratio, chrysotile (Mg₆Si₄O₁₀(OH)₈): CaCO₃ = 1 : 6, was selected on the basis of the decomposition scheme reported in the preceding paper.³⁾ A mixture of 1 mol of chrysotile (Kanto Chemical Co., Inc., 1st grade) and 6 mol of calcium carbonate (Kanto Chemical Co., Inc., 1st grade, mean particle size 6 μm) was prepared. About 10 g of the mixture was mixed with an appropriate quantity of water in a porcelain crucible. This is denoted sample A in Table 1. Sample B was prepared by mixing about 10 g of the asbestos-calcium carbonate mixture with an aqueous solution containing CaCl₂ in a quantity corresponding to 5 mass% of the carbonate.

A sample mixture in a crucible was dried at a controlled temperature of 110°C in air and then heated at a certain temperature (500, 600, 700, 800, 900 or 1000°C) for 2 h in a muffle furnace, followed by cooling gradually to room temperature. For the products of the thermal treatment of samples A and B, powder X-ray diffraction data were obtained with a Rigaku Denki RINT2100V/PC diffractometer.

2.2 Thermal analysis of chrysotile-calcium carbonate systems

As shown in Table 1, samples C–H were made from calcium chloride, mixtures of calcium carbonate and calcium chloride (0, 1 and 5 mass%), and forsterite mixed with calcium carbonate and calcium chloride (in 0 and 5 mass% of carbonate). Forsterite used was obtained by burning chrysotile at 800°C for 2 h. Since chrysotile was decomposed to forsterite, amorphous SiO₂, 1 mol of forsterite in Table 1 contained 1/3 mol of amorphous SiO₂ each. Thermal analysis (with Seiko Instrument, TG/DTA-6300) was performed up to 850°C in an air stream (200 mL/min) at a heating rate of 10°C/min. Samples F, G and H were characterized with a scanning electron microscope (JEOL, JSM-5600) after subjected to thermal analysis.

2.3 Thermodynamic analysis based on thermodynamics data base

Reactions between chrysotile and CaCO₃ were characterized on the basis of the theory of chemical equilibrium by using thermodynamics data base MALT and calculation program of chemical equilibrium gem.^{9)–12)} For a reaction between chrysotile and CaCO₃ in air at atmospheric pressure, the amounts of products in the gaseous, liquid and solid states were calculated at given temperatures. Since the mole ratio of chrysotile to calcium carbonate was 0.5 : 3 in the decomposition scheme of chrysotile, calculation was performed for different quantities of 3, 4 and 5 mol of CaCO₃ and 0.5 mol of chrysotile at each 50° rise in temperature from 227 to 1127°C (500 to 1400 K). Since the calculation results indicated the formation of many

Fig. 1. Powder X-ray diffraction patterns of products obtained by burning a chrysotile–CaCO₃ mixture at different temperatures for 2 h.

gaseous, liquid and solid products, only the major products were plotted in a graph.

3. Results and discussion

3.1 Thermal decomposition of chrysotile with calcium carbonate

Figure 1 shows the powder XRD patterns of products obtained by thermal treatment of sample A at given temperatures for 2 h; up to 900°C were identified only the substances of the original system, such as chrysotile (Mg₆Si₄O₁₀(OH)₈), forsterite (Mg₂SiO₄) derived from chrysotile by dehydration, CaCO₃, and CaO produced from CaCO₃ by elimination of CO₂. Chrysotile is thermally decomposed to forsterite at 700°C. Since this forsterite retains the fibrous shape although it is fragile compared with chrysotile, further decomposition is desired. At 1000°C, substances belonging to the system of formation, such as larnite (Ca₂SiO₄) and MgO, started to be detectable. Thus, chrysotile reacted with CaCO₃ but this reaction required a temperature as high as 1000°C to proceed. This required temperature agreed with that described in the previous reports and patents.

Figure 2 shows the powder XRD patterns of products obtained by heating sample B at certain temperatures for 2 h; up to 600°C only chrysotile and CaCO₃ of the original system were identified, and above 700°C the diffraction peaks of MgO were detected. It was uncertain whether crystalline MgO was formed by crystallization of amorphous MgO produced together with SiO₂ in the course of the thermal decomposition of chrysotile to forsterite, or by separation of MgO as a result of breakdown of the Mg–O–Si lattice that constituted forsterite. At 700°C, as a new product was identified spurrite (Ca₅(SiO₄)₂CO₃) having a diffraction pattern similar to that of forsterite. The identification was made on the basis of the characteristic whether or not diffraction peaks existed at low angles 2θ = 14–30° and around 52°. Above 800°C, larnite (Ca₂SiO₄) was identified.

In summary, the crystal lattice of asbestos could be broken by the use of calcium carbonate only, but a temperature as

Fig. 2. Powder X-ray diffraction patterns of products obtained by burning a chrysotile-CaCO₃ mixture containing CaCl₂ in 5 mass% of CaCO₃ at different temperatures for 2 h.

high as 1000°C was required. In contrast, the addition of a trace of CaCl₂ made it possible to decompose chrysotile at 700°C. The burning products were sintered, but there was no evidence for the formation of melts. The low-temperature decomposition of chrysotile in the CaCl₂-containing reaction systems has been elucidated to be due to the melt formation of CaCO₃-CaO-CaCl₂^{6,7)} and CaO-CaCl₂ phases.⁸⁾ In the present systems studied, however, the quantity of added CaCl₂ was so small that the composition did not correspond to that at the low melting point located in the phase diagrams. The melt formation is, therefore, supposed to be caused by crystalline CaCl₂ that exists locally at a high concentration as a result of precipitation during the drying process from an aqueous CaCl₂ solution.

3.2 Thermal analysis of chrysotile-calcium carbonate systems

Sample C exhibited an endothermic peak due to fusion at 760°C corresponding to the melting point of CaCl₂ and successively a gradual weight loss ascribable to evaporation of CaCl₂ and decomposition of CaCl₂ to CaO. Sample D showed weight loss and heat absorption accompanying elimination of CO₂ from CaCO₃ in a temperature range of 600–750°C. The results of thermal analyses of samples E–H are shown in Figs. 3–6. For these samples, large weight loss and heat absorption due to CO₂ elimination from CaCO₃ obstructed the observation of heat absorption and other thermal phenomena related to the fusion of sample components. For this reason, the samples subjected to the thermal reanalysis were reanalyzed after cooling; the results of the reanalysis are included in the figures. Figures 3 and 4 show the results obtained for samples E and F which contained CaCO₃ and CaCl₂. In Fig. 3, an endothermic phenomenon related to fusion is not observed. In contrast, Fig. 4 exhibits a large endothermic peak at 546°C in addition to small endothermic peaks at 432, 603, 644 and 820°C. At temperatures above 546°C, weight loss occurs which is ascribable to the evaporation of CaCl₂ from the fused phase formed. The foregoing discussion was made by reference to the CaCl₂-CaO phase diagram of Wenz, et al.⁸⁾ and the CaO-CaCl₂-

Fig. 3. Results of (a) thermogravimetric analysis of CaCO₃ mixed with CaCl₂ in 1 mass% and of (b) reanalysis of the same sample after the first run.

Fig. 4. Results of (a) thermogravimetric analysis of CaCO₃ mixed with CaCl₂ in 5 mass% and of (b) reanalysis of the same sample after the first run.

Fig. 5. Results of (a) thermogravimetric analysis of a mixture of chrysotile preheated at 800°C and CaCO_3 , (b) reanalysis of the same sample after the first run, and (c) reanalysis after the second run.

Fig. 6. Results of (a) thermogravimetric analysis of a mixture of chrysotile preheated at 800°C, CaCO_3 and CaCl_2 (in 5 mass% of CaCO_3), (b) reanalysis of the same sample after the first run, and (c) reanalysis after the second run.

CaCO_3 phase diagram of Poletaev et al.,^(6,7) to explain the low decomposition temperature of the chrysotile- CaCO_3 system containing a small quantity of CaCl_2 . On the basis of these diagrams, the CaCl_2 effect described in Section 3.1 was explained by the presence of local areas in which CaCl_2 was concentrated as a result of its precipitation from the aqueous solution during the drying process. This explanation has been confirmed by the present thermal experiments.

Fig. 7. Results of scanning electron microscope (SEM) observation on samples F, G and H after subjected to thermogravimetric analysis: for the sample compositions, see Table 1.

The results of thermal analysis of sample G consisting of forsterite and CaCO_3 are shown in Figs. 5(a, b and c). In a) CO_2 elimination from CaCO_3 is observed, while b) shows a large endothermic reaction peak accompanied by relatively small weight loss at about 422°C, and CO_2 elimination from CaCO_3 . In c) an endothermic peak accompanied by small weight loss appears on a broad endothermic hump. The results of thermal analysis of sample H containing CaCl_2 are shown in Figs. 6(a, b). Thermogram a) exhibits small weight loss and heat absorption at 544°C and CO_2 elimination from CaCO_3 at 730°C. In b) small endothermic peaks accompanied by small weight loss are present at 380 and 583°C on a broad endothermic hump as seen in Fig. 5(c). Thus, we found the phenomenon that a large endothermic peak observed at 422°C for sample G disappeared when CaCl_2 was added, although an endothermic peak of fusion as clear as seen in Fig. 4(b) was not detected.

SEM images observed for samples F, G and H after being subjected to thermal analysis are displayed in Figs. 7(F, G and H). Figure 7(F) is the image of the sample containing CaCl_2 in 5 mass% of CaCO_3 ; CaCO_3 particles having a mean size of about 6 μm originally at the sample preparation adhere to one another. Figure 7(G) shows that the fibrous shape of chrysotile is retained though chrysotile has been converted to forsterite by heating, and CaCO_3 particles maintained the original shape. In Fig. 7(H) for the sample containing CaCl_2 , the surface is covered by adhesives, and a fibrous substance originating from chrysotile cannot be detected.

The SEM observation as well as thermal analysis has demonstrated that the addition of CuCl_2 even in a small amount leads to the formation of melt, which is supposed to allow chrysotile to decompose at a lower temperature as described in the foregoing discussion.

3.3 Thermodynamic analysis with thermodynamics data base

Figure 8 shows the results of calculation of chemical equilibrium for the chrysotile- CaCO_3 system. The major products at each temperature are included in the figure, in which the plots initiate from forsterite (Mg_2SiO_4) and CaCO_3 although the real starting materials are chrysotile and CaCO_3 . Chrysotile is readily decomposed to forsterite, amorphous SiO_2 , and the resulting forsterite retains the fibrous shape. The

Fig. 8. Thermal reaction products predicted on the basis of thermodynamic data base for mixtures of 0.5 mol of chrysotile with various amounts (3, 4 and 5 mol) of CaCO₃ at different temperatures.

decomposition of forsterite is, therefore, important. From this viewpoint, the calculation results are shown for forsterite and its products by plotting their quantities in mole as ordinate and the temperature as abscissa. The theory of chemical equilibrium indicates that forsterite is decomposed at 477°C independently of the quantity of CaCO₃. This result is important for elucidating the fact that the decomposition of asbestos starts at about 600°C in our reaction systems^{2),3)} while the common decomposition temperature reported is of the level of 1000°C.

When 3 mol of CaCO₃ is added for 0.5 mol of chrysotile, Ca₃Mg(SiO₄)₂ and MgO are produced; the addition of 4 and 5 mol of CaCO₃ results in the formation of Ca₂SiO₄ and MgO. In the case of 5 mol of CaCO₃, unchanged CaO is present. Therefore, the ideal mixing ratio predicted from the theory of chemical equilibrium may be 4 mol of CaCO₃ for 0.5 mol of chrysotile.

When the results of burning experiments on chrysotile-CaCO₃ (Fig. 1) are compared with the results of chemical-equilibrium calculation, some discrepancies are found as follows. The calculation indicated the formation of larnite at a temperature slightly below 800°C, but it was not detected until 1000°C in the experiments. Forsterite was decomposed below 500°C in the calculation results, but it was present at 700°C in Fig. 1 and its trace amount still remained at 900°C. For the sample to which CaCl₂ was added (Fig. 2), spurrite (Ca₅(SiO₄)₂CO₃) with a diffraction pattern resembling that of forsterite was identified at 700°C and forsterite was not detected at any temperature. In the case of chrysotile 0.5 mol and CaCO₃ 3 mol, products suggested by the calculation were MgO and Ca₃Mg(SiO₄)₂, but Ca₂SiO₄ was found together with CaO and MgO both in Figs. 1 and 2. The theoretical calculation is based on theory of chemical equilibrium neglecting reaction rate and activation energy completely. In some cases, therefore, the reaction may be governed by the reaction rate even under such a condition that the reaction can proceed according to the theory of chemical equilibrium. In the systems containing a small amount of CaCl₂, the liquid phase of CaCl₂ and CaO are locally formed, allowing a solid-liquid reaction to proceed. As a consequence, the area of interface

between substances in the original system is enlarged so largely that the reaction rate is increased to a great extent. This is thought to be the reason why the experimental results resemble the calculation results obtained under the control of chemical equilibrium even if the real reaction is governed by the reaction rate.

4. Conclusion

Mixtures of chrysotile (Mg₃Si₄O₁₀(OH)₈) and CaCO₃ were burned at temperatures 500 up to 1000°C, and it was found that the decomposition temperature was lowered by the addition of CaCl₂. The effect of added CaCl₂ was supposed to be due to the formation of melts, which was confirmed by thermal analysis and by SEM observation on samples subjected to the thermal analysis. The quantity of CaCl₂ added for the melt formation was different from 75 mol% predicted from the phase diagram, and even the quantity as small as 1–5 mass% of CaCO₃ resulted in the melt formation. Thermodynamic calculation of chemical equilibrium showed that forsterite (Mg₂SiO₄), which was a thermal decomposition product of chrysotile and had a fibrous shape, was decomposed at about 500°C.

In the common decomposition methods to convert asbestos-cement composites to oxides of Ca-Si system, the decomposition proceeds slow because it occurs via a solid-solid reaction; the enhancement of the reaction rate requires the elevation of the reaction temperature above 1000°C. The present study has provided experimental evidence for the supposition that the formation of melts enlarges reaction interface between chrysotile and CaCO₃ so that the decomposition reaction can proceed even at lower temperatures.

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