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Solidification mechanism of allophane by hydrothermal reaction

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ABSTRACT

Solidified materials were prepared by subjecting powder compacts consisting of allophane and slaked lime to hydrothermal reaction at various temperatures. Hydrogarnet was formed after the hydrothermal reaction because of the reaction between allophane and slaked lime. The bending strength of the materials solidified by hydrothermal reaction at 80 °C was greater than 6 MPa. The improvement in the strength of materials by hydrothermal reaction at 80 °C was due to the formation of fine deposits at the surface of allophane aggregates; these deposits filled the spaces between particles of the starting materials. Hydrothermal reaction at temperatures greater than 120 °C resulted in the collapse of the allophane structure, leading to a decrease in the strength of the materials.

1. Introduction

Allophane is a poorly crystalline hydrous alumosilicate in volcanic ash soils. Allophane consists of aggregates of hollow spheres with diameter in the range 3.5–5 nm and has an extremely high specific surface area (Wada, 1981, 1989; Brigatti et al., 2006). Allophane powders have a unique microporous structure, and hence, their potential for use in environmental applications has been studied on the basis of their ion exchange, ion retention, and water holding capacity (Farmer et al., 1984; Onodera et al., 2001; Khan et al., 2006). The solidification of allophane plays an important role in increasing its applications in various fields. However, the strength improvement in specimens sintered at 800 °C using allophane has been reported to be very small (Okada et al., 2008).

The solidification behavior has been studied by subjecting a $CaO–SiO_2–H_2O$ system to a hydrothermal process (Sakiyama and Mitsuda, 1977; Sarkar et al., 2006). Hydrogarnet has been reported to be formed as the major phase when a $CaO–SiO_2–Al_2O_3–H_2O$ system with an $Al/(Al+Si)$ ratio>0.12 is subjected to hydrothermal reaction. The formation of hydrogarnet decreases the strength of the hydrothermally treated materials (Kalousek, 1957; Stebnicka-Kalicka, 1980). We recently prepared solidified materials from kaolinite or metakaolinite by hydrothermal reaction of a $CaO–SiO_2–Al_2O_3–H_2O$ system (Maenami et al., 2000; Maeda et al., 2007). The deposits formed between particles in powder compacts enhance the strength of hydrothermally solidified materials (Maeda et al., in press).

Allophane behaves as an amphoteric ion exchange material because of the presence of both H^+ and OH^- ions on the surface of the particles (Clark and MacBride, 1984). This implies that allophane particles have extremely high surface activity. Our strategy for the solidification of allophane involves increasing its strength through the formation of new deposits on its surface during hydrothermal reaction. The hydrothermal-reaction temperature influences the solubility of the materials. In the present study, we carried out hydrothermal reaction at various temperatures in a $CaO–SiO_2–Al_2O_3–H_2O$ system to solidify materials derived from allophane.

2. Experimental procedure

Allophane isolated from the pumice bed in Kanuma, obtained from the Otsuka Collection (particle size: less than 250 μm, specific surface area: 746 m^2/g) and slaked lime (average particle size: 10 μm, specific surface area: 10 m^2/g) were used as starting materials. X-ray fluorescence (XRF) and thermogravimetric analysis revealed the chemical composition of allophane to be 37.3 mass% of SiO_2, 37.6 mass% of Al_2O_3, 3.1 mass% of Fe_2O_3, 0.7 mass% of CaO, 0.1 mass% of K_2O, 0.4 mass% of TiO_2, 0.2 mass% of MgO, 0.3 mass% of Na_2O, and 20.2 mass% of ignition loss. Lime was prepared by calcining calcium carbonate obtained from Wako Pure Chemical Industries, Ltd. at 1000 °C for 3 h. Slaked lime was obtained by adding distilled water to the prepared lime. The materials were mixed, and the mixture was then added to 40 mass% of distilled water. The $Al/(Al+Si)$ and $Ca/(Al+Si)$ molar ratios were 0.54 and 0.7, respectively. Six hours after the addition to water, the mixture was pressed uniaxially at 30 MPa in a stainless-steel die (15×40 mm). The powder compacts ($4\times15\times45$ mm) were set in a Teflon-lined stainless-steel apparatus (volume: 90 cm^3) and then subjected to hydrothermal reaction under saturated steam pressure (0.05–1.26 MPa) at 80, 120, and 180 °C for 24 h by using 10 cm^3 of distilled water. The materials prepared by hydrothermal solidification at 80, 120, and 180 °C are named samples A, B, and C, respectively.

The flexural strength of the samples ($4\times15\times45$ mm) was estimated by a three-point bending test at a loading rate of 0.5 mm/min. The crystalline phases in the samples were identified by X-ray

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diffraction (XRD) analysis. Infrared spectra of disk-shaped specimens that were prepared from 1 mg of the samples and 500 mg of KBr were obtained using a Fourier-transform infrared spectrometer (FT-IR). The fracture surface morphology was observed by scanning electron microscopy (SEM). The pore size distribution of the samples was determined by mercury intrusion porosimetry. The mesopore size distributions of the samples were obtained by nitrogen gas sorption analysis at −196 °C. The mesopore size distribution curves were calculated by the Barrett–Joyner–Halenda (BJH) method using the desorption isotherms measured by nitrogen gas sorption.

3. Results and discussion

The bending strength of the powder compacts was 1.8 ± 1.0 MPa before the hydrothermal reaction and changed to 6.5 ± 0.1, 3.1 ± 0.2, and 1.1 ± 0.1 MPa after 24 h of hydrothermal reaction at 80, 120, and 180 °C respectively.

Reflections corresponding to slaked lime, calcite, and calcium aluminum oxide hydrate [$Ca_3Al_2O_6 \cdot xH_2O$ ($x = 8$–12), ICDD card No. 2–83] were clearly seen in the XRD pattern before the hydrothermal reaction (Fig. 1). In general, materials with poor crystallinity are metastable to their crystalline counterparts. Calcium aluminum oxide hydrates are assumed to be formed by the reaction of a fraction of allophane with slaked lime after the addition of distilled water. In the XRD pattern of sample A, the reflections corresponding to calcium aluminum oxide hydrate very slightly changed and disappeared after the hydrothermal reaction at temperatures above 120 °C. After the hydrothermal reaction, reflections corresponding to hydrogarnet appeared in the XRD pattern of each sample (Maenami et al., 2000). Hydrogarnet is formed because of the dissolution of allophane, which is the source of aluminum and silicon, and slaked lime, which is the source of calcium. The formation of hydrogarnet in the CaO–SiO_2–Al_2O_3–H_2O system decreases the strength of the material (Kalousek, 1957; Stebnicka-Kalicka, 1980). However, the strength of the materials prepared by hydrothermal solidification at 80 °C increased despite the formation of hydrogarnet. The relative ratios of the reflections corresponding to calcite increased with the hydrothermal temperature. This implies that an increase in the hydrothermal temperature promotes the conversion of slaked lime into calcite due to carbonation.

The FT-IR spectrum of allophane (Fig. 2) showed two absorption bands at around 1000 and 580 cm^{-1}, which were due to the Si–O–Al and Al–O bonds in allophane, respectively (Childs et al., 1990). The spectrum of sample A was almost unchanged after the hydrothermal reaction at 80 °C, indicating that allophane remained in the sample A even after the reaction. In the spectra of samples B and C, the absorption band at around 1000 cm^{-1} shifted toward a lower wavenumber as the hydrothermal-reaction temperature increased, and a shoulder absorption band tended to appear at 1040 cm^{-1}. The band at around 1000 cm^{-1} was reported to shift toward a higher wavenumber with an increase in the Si/Al ratio (Lindner et al., 1998). Under alkaline conditions, the dissolution rate of Al is higher than that of Si (Abidin et al., 2004). The Si/Al molar ratio of the sample before the hydrothermal reaction was determined to be 2.12 by XRF. The Si/Al molar ratios of samples A–C were >2.20. The dissolution of slaked lime during the hydrothermal reaction increased alkalinity in the samples. Therefore, it is proposed that the solubility of allophane increases during the hydrothermal reaction at high temperatures, thereby leading to an increase in the Si/Al ratio. This suggests that the shoulder absorption band at 1040 cm^{-1} is attributable to the Si–O–Al bond in allophane, which partially decomposes because of its dissolution under alkaline conditions. In other words, the solubility of allophane is proposed to be enhanced by hydrothermal reaction at temperatures above 120 °C. The XRD results revealed that hydrogarnet is formed after hydrothermal reaction. The FT-IR spectrum of hydrogarnet, especially that of katoite, shows an absorption band at around 950 cm^{-1} (Passaglia and Rinaldi, 1984). Probably, the hydrogarnet formation and collapse of the allophane structure together cause the absorption band attributed to the Si–O–Al bond in the spectra of samples B and C to shift to a lower wavenumber.

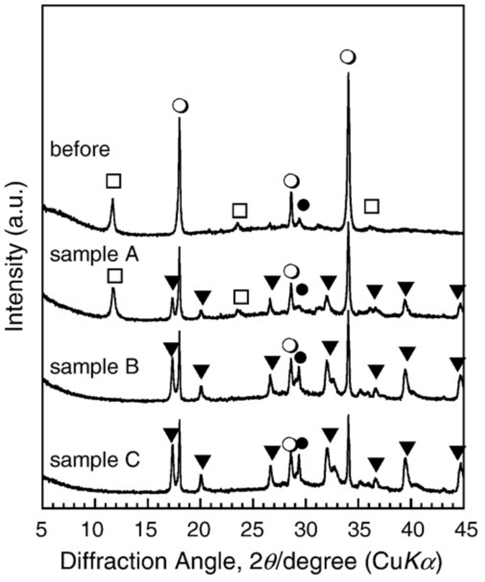

Fig. 1. XRD patterns of the samples before and after the hydrothermal reaction at various temperatures. (▼) hydrogarnet, (●) calcite, (□) calcium aluminum oxide hydrate, and (○) slaked lime.

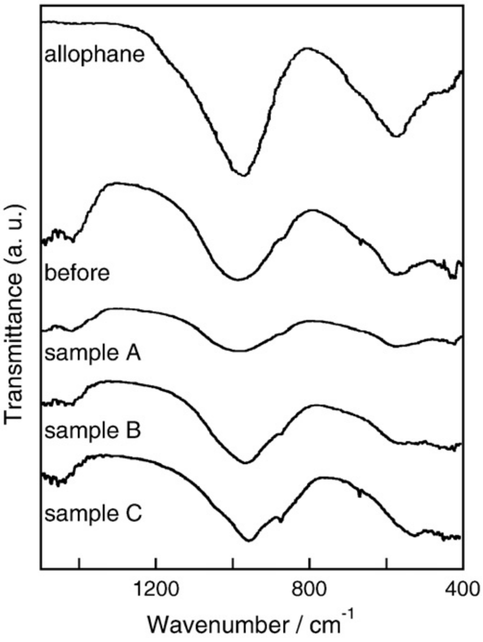

Fig. 2. FT-IR spectra of the allophane and the samples before and after hydrothermal reaction at various temperatures.

Numerous nanoparticles with a diameter of 300 nm can be seen in the SEM micrograph before the reaction (Fig. 3). The SEM micrograph of allophane as a starting material showed nanoparticles with the same diameter of 300 nm, these nanoparticles were considered as allophane aggregates. After the hydrothermal reaction, no allophane-aggregates are seen in any of the micrographs. Some fine deposits were observed in the SEM micrograph of sample A. Spherical deposits with a diameter of ~0.8 µm were observed in the SEM micrograph of sample B. The fracture surface of sample C was completely covered with spherical deposits that have almost the same diameter as those formed on sample B. It appears that the hydrothermal-reaction