

Preparation of CaCO₃ Fibers Coated with Fine Particles of Al(OH)₃

Yoshio OTA, Tetsushi IWASHITA*, Toshihiro KASUGA and Yoshihiro ABE

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi 466

*Yabashi Industries Co., Ltd., 4278-1, Okubo, Akasaka-cho, Ogaki-shi 503-22

Al(OH)₃ 微粒子を被覆した CaCO₃ ファイバーの調製

太田義夫・岩下哲志*・春日敏宏・阿部良弘

名古屋工業大学工学部材料工学科, 466 名古屋市昭和区御器所町

*矢橋工業(株), 503-22 大垣市赤坂町大久保 4278-1

A simple synthetic method for preparing CaCO₃ fibers coated with fine particles of Al(OH)₃ has been developed. A suspension of 3CaO·Al₂O₃·6H₂O-NaOH was prepared by adding Ca(OH)₂ to NaAlO₂ aqueous solution. The CaCO₃ fibers coated with fine particles of Al(OH)₃ were prepared by blowing CO₂ gas into the suspension. They have aspect ratios of ~20 with diameter of ~3 μm. The CaCO₃ fibers coated with fine particles of activated alumina were also obtained by heating them at 500°C. The formed Al(OH)₃ or activated alumina firmly adhered to the CaCO₃ fibers as the substrates.

[Received November 13, 1996; Accepted February 12, 1997]

Key-words : Calcium carbonate, Aluminum hydrate, Fiber, Filler, Carbonation process

1. Introduction

Fillers in the shape of fiber or flake are in great demand for improvement of the mechanical properties of plastic materials.¹⁻³⁾ We have already developed CaCO₃ (aragonite phase) whiskers prepared by a carbonation process using MgCl₂ aqueous solution.^{4,5)} It is known well that alumina trihydrate is a refined mineral filler which offers a bonus of flame retardance and smoke suppression in most plastics applications.⁶⁻⁹⁾ If the CaCO₃ whiskers coated with Al(OH)₃ can be prepared, they should have combined advantages of extenders, fillers for reinforcement, and materials with a function of suppression of flame and/or smoke.

In the present work, we found that CaCO₃ fibers coated with fine particles of Al(OH)₃ are formed by blowing CO₂ gas into the suspension prepared by adding Ca(OH)₂ to NaAlO₂ aqueous solution.

2. Experimental procedure

A suspension was prepared by adding ~37 g of Ca(OH)₂ with stirring into 2 l of aqueous solution in which ~27 g of NaAlO₂ is dissolved to make Ca/Al (in molar ratio) = 1.5 at 60-80°C. Carbon dioxide gas was blown at a flow rate of 0.1 l/min for 0.5-3.25h into the suspension at 25-85°C. The obtained precipitates were gathered by filtration, and then were washed in water and dried at ~100°C. They were heated at 300-1200°C for 10 min. Powder X-ray diffraction (XRD) (Cu Kα, 30 kV, 15 mA) analysis was conducted to identify the crystalline phases of the precipitates and the heated ones. Their morphologies were observed with scanning electron microscope (SEM), incorporating energy dispersive X-ray (EDX) microanalyzer. The measurements of N₂-adsorption isotherm were conducted to estimate their BET surface areas. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in air at a heating rate of 10°C/min.

3. Results and discussion

Figures 1 and 2 show XRD patterns of the precipitates obtained by introducing Ca(OH)₂ and CO₂ gas to NaAlO₂ aqueous solution and their SEM photographs, respectively. The suspension containing polyhedral 3CaO·Al₂O₃·6H₂O (C₃AH₆) was prepared firstly by adding Ca(OH)₂ into

NaAlO₂ aqueous solution (Figs. 1(a) and 2(a)). It is known that C₃AH₆ is usually obtained by the hydration of 3CaO·Al₂O₃ (C₃A) which is formed by heating a mixture of CaCO₃ and Al₂O₃ at high temperature (~1300°C).¹⁰⁾ In the present work, C₃AH₆ was obtained by adding Ca(OH)₂ into NaAlO₂ aqueous solution. The reaction equation may be presented as follows:

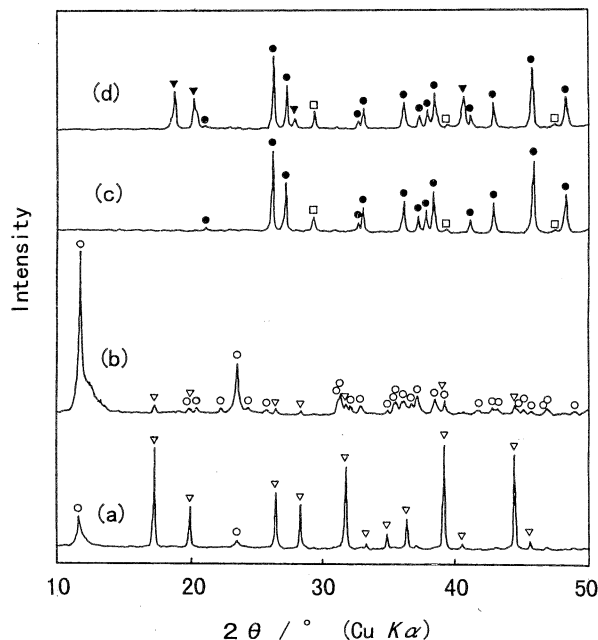
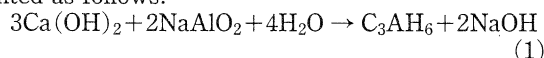


Fig. 1. XRD patterns of the precipitates obtained by introducing ~37 g of Ca(OH)₂ and CO₂ gas at a flow rate of 0.1 l/min to 2 l of ~27 g NaAlO₂ aqueous solution. (a) before the CO₂-gas-blowing, (b) after the CO₂-gas-blowing for 0.5h at 80-85°C, (c) after the CO₂-gas-blowing for 2.25h at 80-85°C, (d) after the CO₂-gas-blowing for 2.25h at 80-85°C and the subsequent blowing for 1h at 25-30°C.

● CaCO₃ (aragonite), □ CaCO₃ (calcite), ○ C₃A·CaCO₃·11H₂O, ▼ Al(OH)₃ (bayerite).

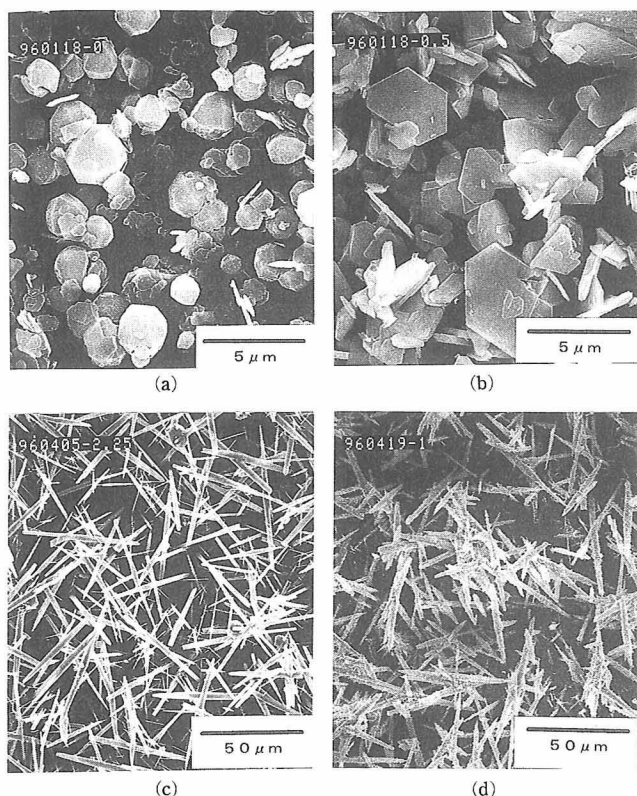
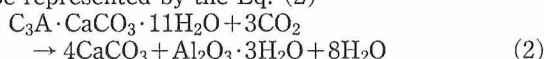


Fig. 2. SEM photographs of the precipitates shown in Fig. 1. Precipitates (a)–(d) were prepared with conditions of (a)–(d) in Fig. 1, respectively.

When CO_2 gas was blown into this suspension at 80–85°C, platelike $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ ($\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$) were precipitated by blowing CO_2 gas for ~ 0.5 h (Figs. 1(b) and 2(b)) and subsequently CaCO_3 (aragonite phase) fibers were precipitated by blowing CO_2 gas for ~ 2.25 h (Figs. 1(c) and 2(c)). Carlson and Berman reported that $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ in aqueous suspension is not stable in the presence of carbon dioxide and the decomposition may be represented by the Eq. (2)¹¹⁾



The suspension containing $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ is obtained by blowing CO_2 gas into the C_3AH_6 – NaOH suspension. On blowing CO_2 gas, the $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ in the suspension is decomposed. As NaOH is contained in the suspension, $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ may not be precipitated as shown in Eq. (2). As a result, only CaCO_3 is precipitated in NaAlO_2 aqueous solution. The CaCO_3 was almost aragonite phase.

Although the aragonite was precipitated at temperature range in this work (i.e., 25–85°C), their size and aspect ratio were increased with increasing temperature.

After the temperature of the CaCO_3 fibers– NaAlO_2 suspension was decreased to 25–30°C from 80–85°C, CO_2 gas was blown for 1h into the suspension. The resultant fibrous products consist of aragonite and bayerite (Figs. 1(d) and 2(d)). When CO_2 gas was blown into the suspension containing the aragonite fibers at high temperature of 80–85°C, the fibers were not coated homogeneously with $\text{Al}(\text{OH})_3$ and the formed $\text{Al}(\text{OH})_3$ particles were larger in size than those obtained at 25–30°C. Although the reason was not clear, the optimum temperature for the $\text{Al}(\text{OH})_3$ -coating was found to be $\sim 25^\circ\text{C}$. Figure 3(a) shows a SEM photograph of the surface of a fiber shown in Fig. 2(d) and the corresponding elemental X-ray map of aluminum (Fig. 3(b)). Figure 3(c) shows a SEM photograph of the fracture face of the fiber. These observations reveal that numerous fine particles of $\text{Al}(\text{OH})_3$ are formed on the surface of the CaCO_3 fiber. Crystalline phases in which are precipitated at the process in the present work are summarized in Fig. 4.

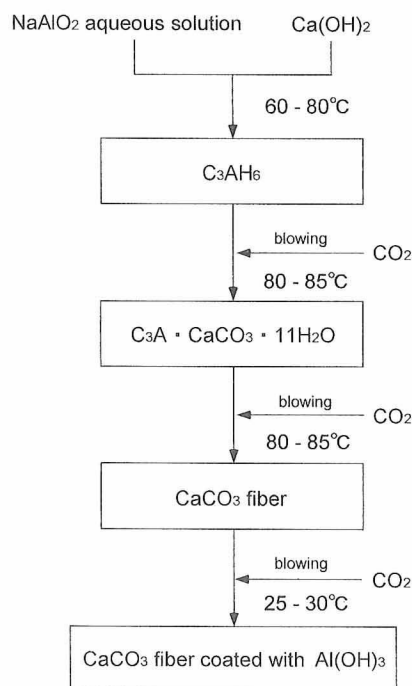


Fig. 4. Change in precipitates in the suspension until formation of CaCO_3 fibers coated with fine particles of $\text{Al}(\text{OH})_3$.

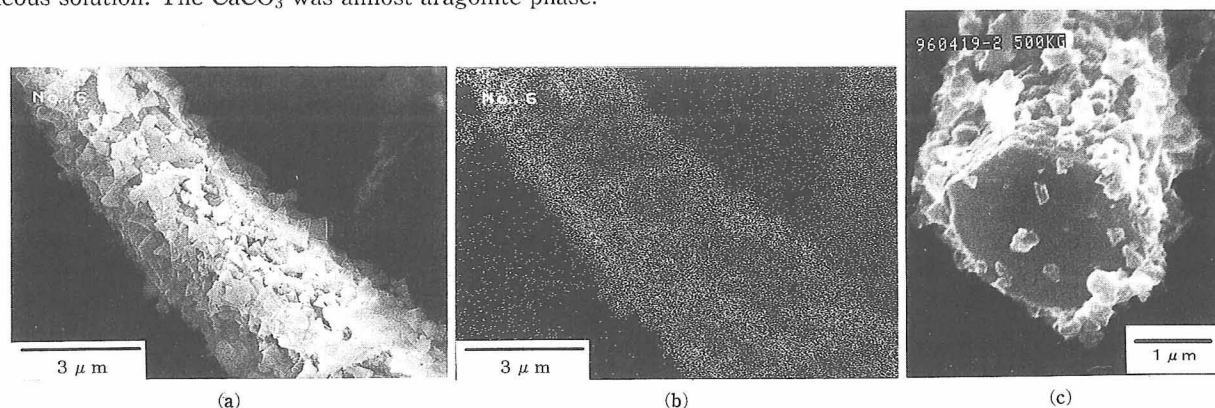


Fig. 3. SEM photographs of (a) the surface of a fiber obtained by the condition shown in Fig. 1(d), (b) the corresponding elemental X-ray map of aluminum, and (c) the fracture face of a fiber obtained under the condition shown in Fig. 1(d).

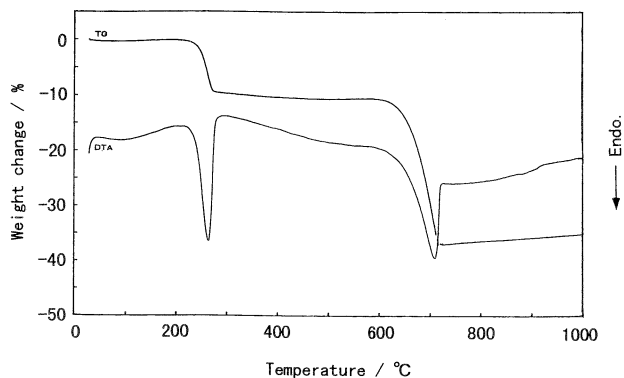


Fig. 5. TGA and DTA curves for the CaCO₃ fibers coated with fine particles of Al(OH)₃.

Figure 5 shows TGA and DTA curves for the CaCO₃ fibers coated with fine particles of Al(OH)₃. The large weight decreases in the TGA curve are seen at temperature ranges of 220–280°C and 600–720°C. The two endothermic peaks due to the decreases are seen in the DTA curve. When alumina trihydrate is heated to temperatures above about 220°C, it changes to alumina by losing 34.6 mass% of water.⁸⁾ The weight decrease of the obtained products is ~10 mass% at 200–300°C. Assuming that the decrease is due to dehydration of the formed Al(OH)₃, the amount of Al(OH)₃ in the fibrous products obtained is estimated as ~30 mass%. The weight decrease at a temperature of >~600°C, which is accompanied by endotherm, is due to decomposition of CaCO₃ into CaO and CO₂.

When the CaCO₃ fibers coated with fine particles of Al(OH)₃ were heated at 500°C for 10 min, they were changed to CaCO₃ fibers coated with fine particles of activated alumina. All peaks in the XRD pattern of the products agreed with those of calcite. Their specific surface area (123 m²/g) was much larger than that of the parent CaCO₃ fibers (2.5 m²/g) since they were coated with fine activated alumina. Since the activated aluminas are widely used as adsorbents, desiccants, catalysts and catalyst supports,¹²⁾ it is expected that the CaCO₃ fibers coated with activated alumi-

na are also applicable to such fields. The coated fibers were treated strongly in an ultrasonic water bath. In spite of the treatment, Al(OH)₃ or activated alumina still adhered to the CaCO₃ fiber.

4. Summary

A suspension of C₃AH₆-NaOH was prepared by adding ~37 g of Ca(OH)₂ with stirring into 2 l of aqueous solution in which ~27 g of NaAlO₂ is dissolved. The CaCO₃ fibers having aspect ratios of ~20 with diameters of ~3 μm were obtained by blowing CO₂ gas into the suspension at 80–85°C. Successive CO₂-gas-blowing at 25–30°C leads to precipitation of the fine particles of Al(OH)₃ on the surface of the CaCO₃ fibers, so that the CaCO₃ fibers coated with fine particles of Al(OH)₃ were obtained. By heating them at 500°C, the CaCO₃ fibers coated with fine particles of activated alumina with large specific surface area of ~120 m²/g were also obtained. These coated layers firmly adhered to the CaCO₃ fibers.

References

- 1) A. Kelly and W. R. Tyson, "High Strength Materials," John Wiley & Sons, Inc. (1965) pp. 579–602.
- 2) T. T. Wu, *Int. J. Solids Structures*, 2, 1–8 (1966).
- 3) T. H. Ferrigno, "Handbook of Fillers and Reinforcements for Plastics," Ed. by H. S. Katz and J. V. Milewski, Van Nostrand Reinhold Co. (1978) pp. 11–58.
- 4) Y. Ota, S. Inui, T. Iwashita, T. Kasuga and Y. Abe, *J. Am. Ceram. Soc.*, 78, 1983–84 (1995).
- 5) Y. Ota, S. Inui, T. Iwashita, T. Kasuga and Y. Abe, *J. Ceram. Soc. Japan*, 104, 196–200 (1996).
- 6) W. J. Connolly and A. M. Thornton, *Mod. Plastics*, 43, 154–202 (1965).
- 7) R. C. Hopkins, *Polymer Age*, 6, 130–35 (1975).
- 8) E. A. Woycheshin and I. Sobolev, "Handbook of Fillers and Reinforcements for Plastics," Ed. by H. S. Katz and J. V. Milewski, Van Nostrand Reinhold Co. (1978) pp. 234–49.
- 9) J. Z. Keating, *J. Fire Retardant Chemistry*, 9, 215–20 (1982).
- 10) R. Turriziani, "The Chemistry of Cements," Vol. 1, Ed. by H. F. W. Taylor, Academic Press (1964) pp. 233–86.
- 11) E. T. Carlson and H. A. Berman, *J. Res. Nat. Bur. Stand.*, 64A, 333–41 (1960).
- 12) K. A. Evans and N. Brown, *Spec. Publ. R. Soc. Chem.*, No. 40, 164–95 (1981).