JOURNAL OF MATERIALS SCIENCE 27 (1992) 6193–6196

Preparation of transparent mullite–silica film by heat-treatment of imogolite

N. DONKAI, T. MIYAMOTO, T. KOKUBO
Institute for Chemical Research, Kyoto University, Gokasyo, Uji, Kyoto, 611, Japan
H. TANEI
Production Engineering Research Laboratory, Hitachi Ltd, 292, Yoshida-cho, Totsuka-ku, Yokohama, Kanagawa, 244, Japan

Natural gel-like imogolite was dispersed in an acetic acid aqueous solution. An imogolite film was prepared by evaporating the solvent from the imogolite solution and then subjecting it to heat-treatment. It transformed to an amorphous film at around 500 °C and then to a mullite–silica composite film at around 1000 °C without giving pore and cracks. The film heat treated to 1200 °C showed high transparency as well as a low thermal expansion coefficient of about 4×10^{-6}.

1. Introduction

Imogolite is a unique paracrystalline alumina–silicate first found in volcanic ash-derived soils in Japan [1, 2]. Imogolite yields broad characteristic X-ray diffraction peaks [1] and appeared under an electron microscope as a rod-like tube, several micrometres in length and 2–2.5 nm in diameter [2, 3]. Cradwick *et al.* [4] proposed that the wall of the imogolite tube consists of a cylindrical single sheet of gibbsite where the inner hydroxyls are replaced by orthosilicate groups and the chemical composition is given by $(OH)_3{\cdot}Al_2O_3{\cdot}SiOH$ or $Al_2O_3{\cdot}SiO_2{\cdot}2H_2O$, as shown schematically in Fig. 1. Synthesis of imogolite has been studied and attempts to produce material matching the naturally occurring samples have succeeded [5–7].

Thermal analyses of imogolite have been carried out by Yoshinaga and Aomine [1], and their results showed that the imogolite structure was decomposed with dehydroxylation on heating to 450 °C. An exothermic peak was also observed around 950 °C in differential thermal analysis (DTA), which was thought to correspond to the formation of γ-alumina. The authors studied the X-ray diffraction pattern of mullite crystal when imogolite was heat treated at 1200 °C.

Mullite ($3Al_2O_3{\cdot}2SiO_2$) is an extensively investigated crystalline phase in the Al_2O_3–SiO_2 binary system and its sintered material is known to possess a good high-temperature mechanical property and low thermal expansion. Mullite–silica composites are expected to show similar characteristics.

Imogolite can be dispersed monomolecularly in acidic aqueous solution [8], and thus the film is easily prepared by casting the solution. Heat treatment of the imogolite film is expected to give a mullite–silica composite. In the present study, structural change of the imogolite film by a heat treatment as well as some properties of the heat-treated film were investigated.

2. Experimental procedure

Gel-like imogolite was collected from a pumice bed at Murasakino (Kitakami, Iwate-ken, Japan). Imogolite gels were treated first with $Na_2S_2O_4$–$NaHCO_3$–$Na_3C_6H_5O_7{\cdot}2H_2O$ at 80 °C to extract inorganic impurities and then with Na_2CO_3 to remove amorphous silicates. Organic impurities were disintegrated with 30% H_2O_2 at 80 °C and washed out with water. Colourless imogolite gel thus obtained was washed further in a soxhlet extractor with hot acetic acid aqueous solution (1.2 vol %, pH 3.0) for 1 week.

Imogolite gel was dispersed in acetic acid aqueous solution at pH 3.0 by applying a 20 kHz ultrasonic wave for 30 min. The undissolved portion in the solution was separated by centrifugation at 10 000 r.p.m. for 1 h, and the supernatant was concentrated with an evaporator to a concentration of approximately $0.5\ \mathrm{g\,dl^{-1}}$. The solution was filtered through an ultracella-filter membrane of pore size 0.2 μm. Intrinsic viscosity, η, of the imogolite thus prepared was $2.7\ \mathrm{dl\,g^{-1}}$ and the weight average molecular weight, M_w, was estimated using the previously established relation [8] between η and M_w as 2.0×10^6, which corresponds to the imogolite tube length of 420 nm.

A film was prepared by placing the imogolite solution in a disc-type vessel made of teflon and evaporating the solvent gradually at room temperature. Thermogravimetric (TG) and DTA measurements of crushed imogolite powder were carried out in ambient atmosphere from room temperature to 1300 °C at a heating rate of $5\ ^{\circ}\mathrm{C\,min^{-1}}$, using a TG–DTA System 001 Equipment (MAC Science Co., Tokyo, Japan). The imogolite cast films were heated to various temperatures below 1600 °C at a rate of $5\ ^{\circ}\mathrm{C\,min^{-1}}$ and held for various periods at the respective temperature and then examined by Fourier transform-infrared spectroscopy (FT-IR, JASCO 8000-type, Japan Spectroscopic Co., Ltd, Tokyo, Japan), X-ray diffraction

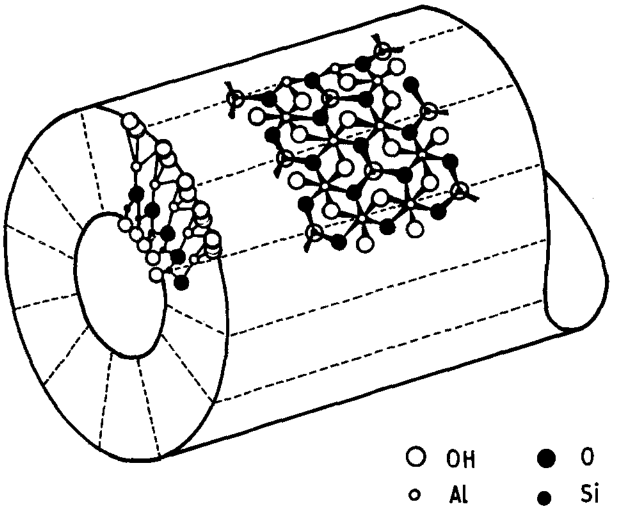

Figure 1 Schematic view of paracrystalline imogolite tube.

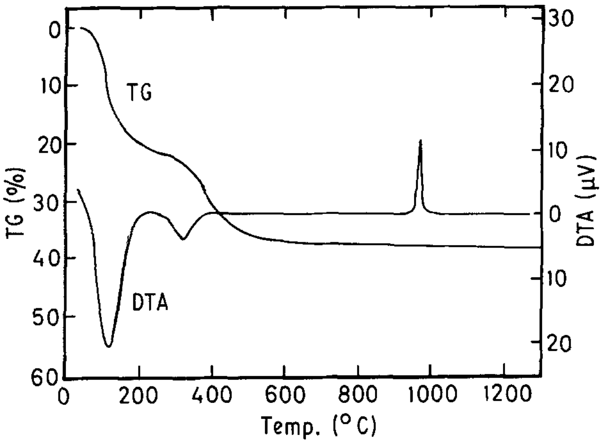

Figure 2 Thermogravimetric and differential thermal curves of imogolite.

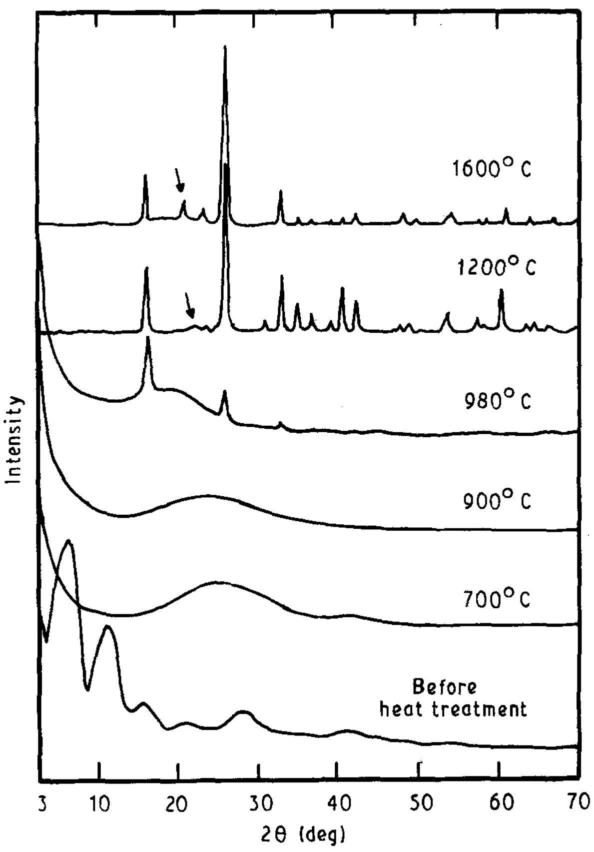

Figure 3 X-ray diffraction patterns of imogolite films heat treated at various temperatures up to 1600 °C. Samples heat treated at 1200 and 1600 °C were held for 2 h at the respective temperature, and the sample at 980 °C was held for 10 h. Arrows indicate the diffraction peaks due to tridimite. All other peaks are assigned to mullite.

(RINT-type, Rigaku Co., Osaka, Japan), and scanning electron microscopy (SEM, S-510 type, Hitachi Co., Ibaragi, Japan).

Because it was difficult to make a thick film using this casting method, the thicker imogolite film was prepared by kneading imogolite powder with a small amount of water and then pressing it with a pressure of 0.6 ton cm^{-2}. Here fine imogolite powder was obtained by a freeze-dried method from the dilute solution. Thermal expansion was measured with this thicker film after heat treatment at 1200 °C, using a laser interferometry thermal expansion meter LIX-1 type (Shinku-riko Co., Tokyo, Japan).

3. Results and discussion

3.1. TG and DTA

The results of TG and DTA measurements are shown in Fig. 2. The weight loss of 35% upto 500 °C is attributed to the loss of absorbed water and dehydroxylation which correspond, respectively, to the endothermic peaks in DTA at 130 and 330 °C. Our results are similar to those reported by other investigators [1, 2], except that the endothermic peak position at 330 °C is lower than the reported position at 420–440 °C. We also observed an exothermic peak at 967 °C. The origin of this peak will be discussed in a following section on the basis of the X-ray diffraction results.

3.2. X-ray diffraction analysis

X-ray diffraction patterns were taken from imogolite film heat treated at various temperatures up to 1600 °C and the results are given in Fig. 3. The characteristic diffraction peaks of imogolite have been reported to disappear by heating at 500–600 °C [1]. Our results suggest that imogolite film decomposes to become amorphous around 500 °C and then mullite crystallization takes place around 1000 °C. The X-ray diffraction of imogolite film heat treated at 980 °C for 10 h, just above the exothermic peak temperature of 967 °C, exhibited only peaks due to mullite crystal in an amorphous phase, and not those due to Al–Si spinel or γ-alumina. Heat treatment of the imogolite film at 1200 °C for 2 h yielded diffraction peaks corresponding totally to mullite crystal, except for the weak peaks at $2\theta = 21.3^\circ$ and 22.0° which may be assigned to the formation of tridimite because of the excess amount of SiO_2 in imogolite compared to the stoichiometric mullite composition. The film heat treated at 1600 °C for 2 h also showed the mullite diffraction pattern contaminated with tridimite. These results show that imogolite is transformed to the mullite–silica composite by heat treatment.

3.3. Infrared spectra

Imogolite shows two characteristic absorptions at 950 and 990 cm^{-1} due to Si–O and Al–O stretching, as seen in Fig. 4. These peaks shift in the region between 1100 and 1200 cm^{-1} on heating the imogolite film to 1000 °C. Infrared spectra of imogolite films heat treated above 1200 °C coincide with those of mullite, showing the absorption due to four-coordinated Al–O and Si–O at 1180 and 1120 cm^{-1}, respectively. The infrared spectrum was measured for pure mullite (MP-20, Chichibu Cement Co. Ltd) and is also given in Fig. 4 for comparison.

3.4. Microstructure of heat treated imogolite film

Imogolite cast films were prepared with about 100 μm thickness, which were optically transparent. Fig. 5 shows a scanning electron micrograph of the fractured surface of the imogolite film as-prepared, where the film surface is seen on the left side and the fractured surface on the right. This cast film was heat treated at 1200 °C for 2 h to achieve mullitization, which was confirmed from the X-ray diffraction pattern. The film was optically transparent even after heat treatment. Fig. 6 shows scanning electron micrographs taken from the fractured edge surface. The characteristic feature is the closely stacked lamellar structure. This may be the result of agglomeration and development of the lamellae shown in Fig. 5 for the as-cast film. The high-magnification photograph (Fig. 6b) suggests no exaggerated granular growth in the film heat treated at 1200 °C. Although a weight loss of 35% was evaluated on heating up to 1200 °C in TG measurement, the film structure after heat treatment was relatively dense and no cracking was observed by SEM. Fig. 7 shows the film surface heat treated at 1600 °C for 2 h, and the

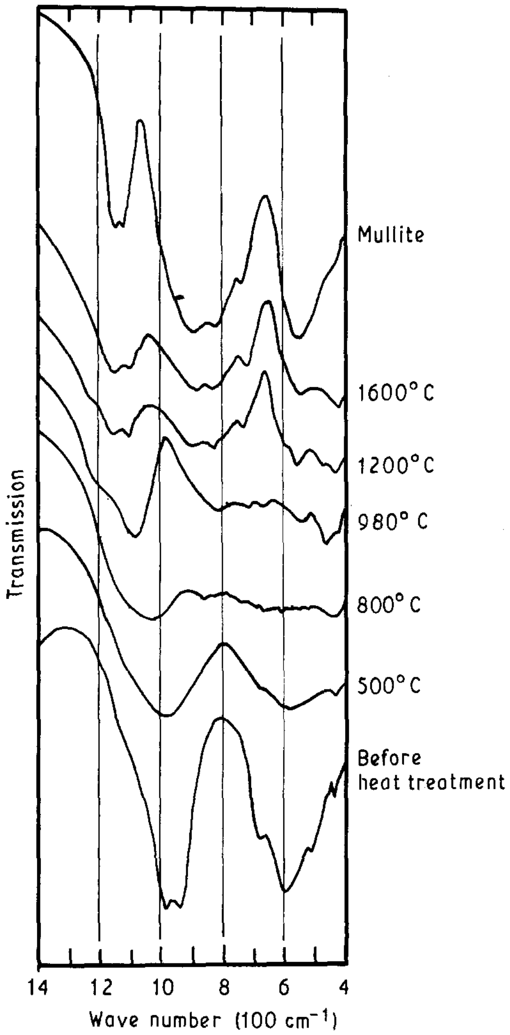

Figure 4 Infrared transmission spectra of imogolite films heat treated at various temperatures.

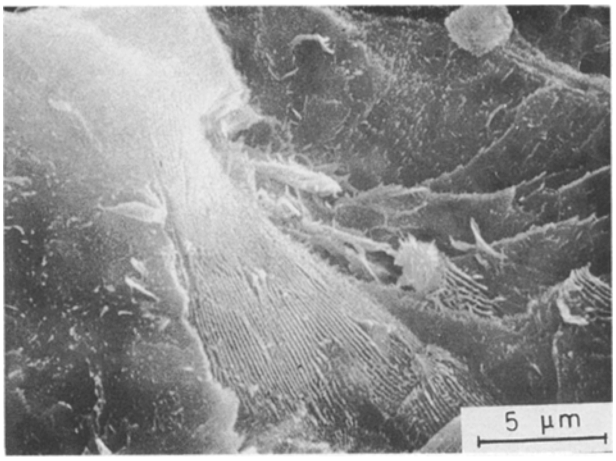

Figure 5 Scanning electron micrograph of imogolite cast film.

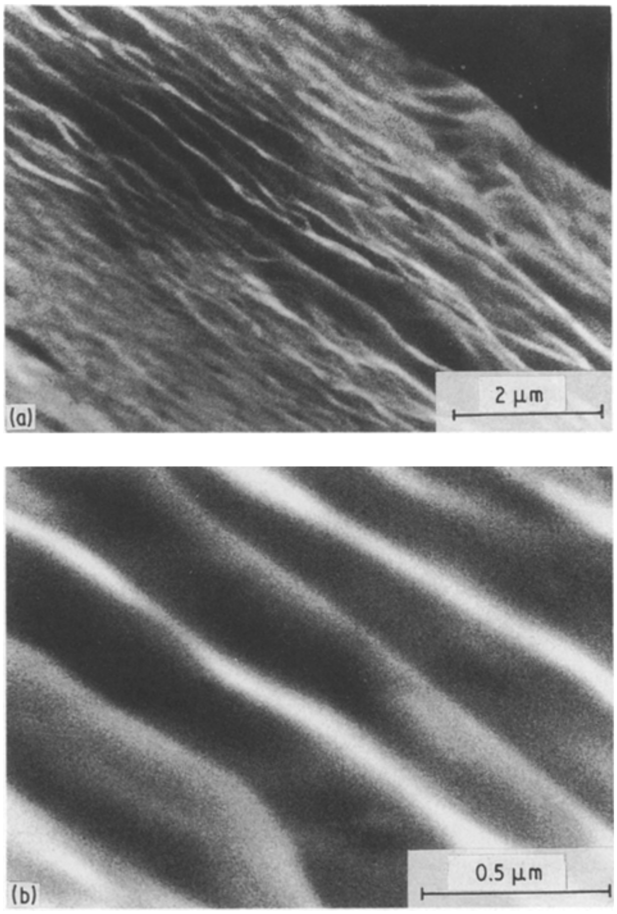

Figure 6 (a) Scanning electron micrograph of imogolite film heat treated at 1200 °C for 2 h. (b) High-magnification photograph of part of (a).

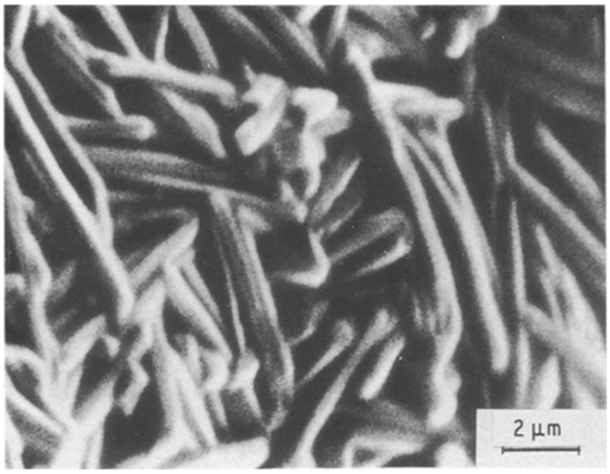

Figure 7 Scanning electron micrograph of imogolite film surface heat treated at 1600 °C for 2 h.

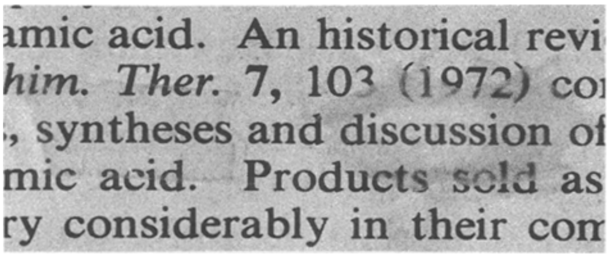
ımic acid. An historical revi
him. Ther. 7, 103 (1972) coı
., syntheses and discussion oi
mic acid. Products sold as
ry considerably in their con

Figure 8 Photographs visualizing the imogolite film transparency. The words 'syntheses" and "discussion" were totally covered with as-cast and heat-treated (1200 °C) film, respectively.

fractured surface also shows the same needle-like structure. Davis and Pask [9] pointed out that sintering the Al_2O_3–SiO_2 powder in the absence of a liquid phase yields mullite with a chunky granular shape, whereas rapid cooling from the liquid phase forms a needle-like shape. On the other hand, Matsuo *et al.* [10] showed that the composite of mullite and silica glass produced a needle-like crystal with increasing SiO_2 content. Because imogolite has an excess amount of SiO_2 compared to the stoichiometric mullite composition, the needle-like crystalline growth observed in Fig. 7 may be attributed to the same mechanism as that reported by Matsuo *et al.*

3.5. Optical and thermal properties of heat-treated imogolite films

Imogolite film was transparent after heat treatment at 1200 °C for 2 h, while the film heat treated at 1600 °C was opaque. The transmittance of visible light was measured for the cast and the heat-treated imogolite films at 1200 °C in the wavelength range 400–800 nm, and the results were 50% and 38% for the former (70 μm thick) and the latter film (65 μm thick), respectively, independent of the wave length investigated here. Fig. 8 shows a photograph taken where the words "syntheses" and "discussion" were covered totally with the as-cast and the heat-treated (1200 °C) film, respectively. The transparency is sufficient to read the words. Infrared measurements showed that the imogolite films heat treated at higher than 1000 °C possessed no specific absorption between 4600 and 1500 cm^{-1} (2.2–6.6 μm wavelength).

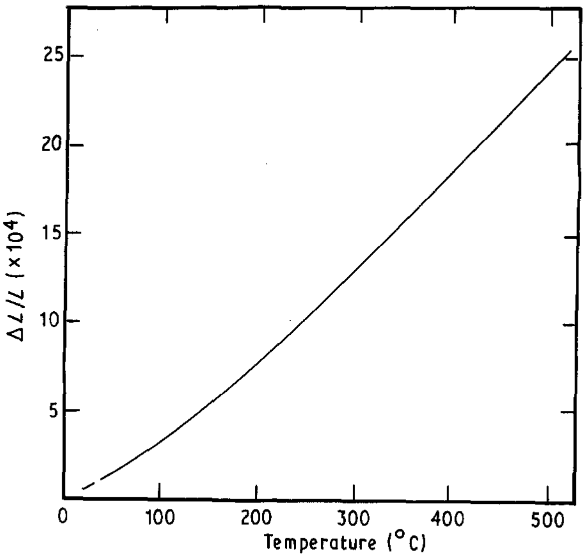

Figure 9 Linear thermal expansion ($\Delta L/L$) of imogolite film heat treated at 1200 °C for 2 h, where ΔL and L are the expansion length and the length of the original sample, respectively.

The thermal expansion was measured with a thicker imogolite film heat treated at 1200 °C and the result is shown in Fig. 9. The linear thermal expansion coefficients, α, were evaluated as 2.95, 3.44, 3.76, 3.95 and 4.12×10^{-6}, respectively, at temperatures, 100, 200, 300, 400 and 500 °C. These values are slightly smaller than that reported for pure mullite (4.0×10^{-6}).

References

1. N. YOSHINAGA and S. AOMINE, *Soil Sci. Plant Nutr.* (*Tokyo*) **8** (1962) 22.
2. K. WADA, *Develop. Sedimentrogy* **26** (1978) 147.
3. K. WADA, N. YOSHINAGA, H. YOTSUMOTO, K. IBE and S. AIDA, *Clay Miner.* **8** (1970) 487.
4. P. D. G. CRADWICK, V. C. FARMER, J. D. RUSSELL, C. R. MASSON, K. WADA and N. YOSHINAGA, *Nature Phys. Sci.* **240** (1972) 187.
5. S.-I. WADA, A. ETO and K. WADA, *J. Soil Sci.* **30** (1979) 347.
6. V. C. FARMER and A. R. FRASER and J. M. TAIT, *J. Chem. Soc. Chem. Commun.* (1977) 462.
7. V. C. FARMER and A. R. FRASER, *Develop. Sedimentrogy* **27** (1979) 547.
8. N. DONKAI, H. INAGAKI, K. KAJIWARA, H. URAKAWA and M. SCHMIDT, *Makromol. Chem.* **186** (1985) 2623.
9. R. F. DAVIS and J. A. PASK, in "High Temperature Oxides", Part IV, edited by A. N. Alper (Academic Press, New York, 1971) p. 37.
10. Y. MATSUO, K. MINAMISAWA, K. YASUDA and S. KIMURA, in "Preprint of Meeting of Basic Ceramic Science", Japan, Vol. 28 (1990) p. 35.

Received 15 October 1991
and accepted 17 February 1992