Journal of the European Ceramic Society 20 (2000) 397–402

Synthesis of needlelike mullite particles using potassium sulfate flux

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Received 23 March 1999; received in revised form 24 June 1999; accepted 3 July 1999

Abstract

When a powder mixture consisting of $Al_2(SO_4)_3$, K_2SO_4 and SiO_2 was heated in an alumina crucible covered with a lid, aggregations of needlelike mullite particles were obtained. The effects of the mixing ratio of the raw materials and of the heating temperature on the synthesis and morphology of the needlelike mullite particles were investigated. When the powder mixture consisting of 24.5 mol% of $Al_2(SO_4)_3$, 48.0 mol% of K_2SO_4 and 27.5 mol% of SiO_2 was heated at 1100°C for 3 h, the mullite particles were 0.2–0.5 μm in width and 2–5 μm in length, resulting in a specific surface area of the mullite particles of 136 m^2/g. The formation process of these mullite particles was discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Flux growth; Mullite; Aspect ratio; Potassium sulfate

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$), which is the only stable aluminosilicate phase in the Al_2O_3–SiO_2 binary system at atmospheric pressure, is expected to be a high temperature structural materials due to the high melting point (1890 ± 10°C).[1] good creep resistance,[2] low-thermal expansion,[3,4] and the excellent mechanical property whereby the flexural strength does not decrease even at temperatures as high as approximately 1300°C.[5] Mullite whiskers have attracted considerable attention as a reinforcement to enhance the mechanical and thermal properties for metal or ceramic materials. Several methods for synthesizing mullite fibers or whiskers have been reported. For example, Ismail et al.[6] prepared mullite whiskers by heating a mullite precursor sol, which was prepared beforehand by mixing boehmite and silica sols and then reacting the obtained sol with HF, at 1400°C for 1 h. Okada et al.[7] synthesized mullite whiskers by a vapor-phase-reaction at 1100–1600°C using a mullite composition xerogel and AlF_3. Moyer et al.[8] reported a method of synthesizing mullite whiskers by reacting mixtures of alumina and silica in SiF_4 at 1100°C. Chen et al.[9] prepared transparent mullite fibers using aluminum carboxylates (ACs) and tetraethyl orthosilicate (TEOS). Li et al.[10] heated a mixture consisting of ammonium alum and hydrated halloysite clay at 1500°C for 10 h and treated the mixture with hydrofluoric acid after heating to produce mullite whiskers.

Needlelike mullite particles as well as mullite whiskers (fibers) are expected to be used as a reinforcement in high-temperature structural materials. Recently, the flux method of obtaining ceramic needle crystals,[11] fibers[12] and whiskers[13] has attracted significant attention due to the increased crystal yield and the formation of uniform crystals provided by this method. In the present study, a novel synthetic method of obtaining needlelike mullite particles that involves the use of potassium sulfate flux,[13] which is used in fabricating aluminum borate whiskers,[13] was investigated. The optimum synthetic condition and the formation process of needlelike mullite particles were investigated.

2. Experimental procedures

As raw materials, aluminum sulfate hydrate [$Al_2(SO_4)_3 \cdot 14$–$17H_2O$], and silica (flake-like amorphous, mean particle diameter: 10 μm) of reagent grade and potassium sulfate (K_2SO_4, above 99%) flux were used. The aluminum sulfate hydrate was calcined at 300°C for 12 h to form $Al_2(SO_4)_3$. Each of the starting powder mixtures (approximately 7 g), containing various ratios of the raw materials, was placed into an

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PII: S0955-2219(99)00180-6

alumina crucible (70 mm high, 50 mm diameter) and was covered with a lid. The crucible was heated in a muffle furnace having SiC electric heating elements at 700–1200°C for 3 h. The heating rate was 10°C/min. The heating program was monitored by an automatic controller having a thermocouple of Pt–13%Rh. After heating at the selected temperature for 3 h, the power was shut off and the crucible was then cooled in the furnace to room temperature. As an example, Fig. 1 shows the thermal history for a starting powder mixture that was heated at 1000°C for 3 h. A reactant mass, remaining at the bottom of the crucible, was dissolved with 1 N HCl at 70–80°C for 0.5–1 h. As a result, white and opaque particles were obtained as final products. Crystalline phase and morphology of the particles were examined by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM), respectively. In order to elucidate the formation process of the needlelike mullite particles, differential thermal analysis (DTA) and thermogravimetric analysis (TG) for a starting powder mixture were performed at temperatures of up to 1200°C at a heating rate of 10°C/min in air. Finally, in order to characterize the needlelike mullite particles, the specific surface area of the particles was measured by the BET method using nitrogen absorption.

3. Results and discussion

3.1. Synthesis of needlelike mullite particles

The starting powder mixtures which yield only mullite crystal were investigated. Powder mixtures of $Al_2(SO_4)_3$:K_2SO_4 = 1:1.96 (mol%) were mixed at various ratios with SiO_2 to prepare starting powder mixtures. Fig. 2 shows the XRD patterns of the samples obtained by heating the starting powder mixtures at 1000°C. Peaks indicating mullite crystal were detected for the samples. When the starting powder mixture containing 19.2 mol% of SiO_2, which is the ideal composition for mullite, was heated, small intensity peaks of Al_2O_3 crystal were also detected. The formation reaction of mullite seemed not to have occurred completely. Diffraction peak patterns indicating only mullite crystalline phase were observed for the samples obtained by heating the starting powder mixtures containing more than 27.5 mol% of SiO_2. The peak intensities of mullite were weakened with increasing SiO_2 in the starting powder mixtures. However, the diffraction peak angles of mullite did not change with increasing SiO_2 and corresponded to those of the ideal mullite composition, so

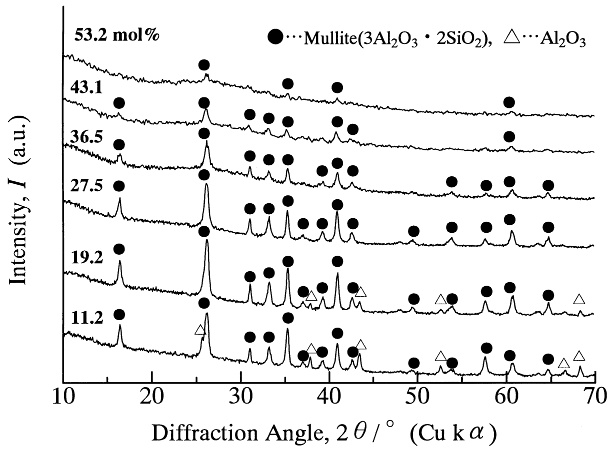

Fig. 2. XRD patterns of the samples obtained by heating powder mixtures consisting of $Al_2(SO_4)_3$: K_2SO_4:SiO_2 = 1:1.96: X (mol%) at 1000°C for 3 h and then treating with hot 1 N HCl.

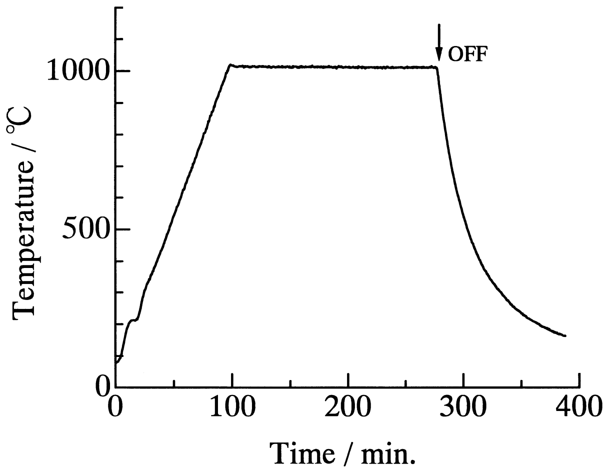

Fig. 1. Thermal history for a starting powder mixture that was heated at 1000°C for 3 h.

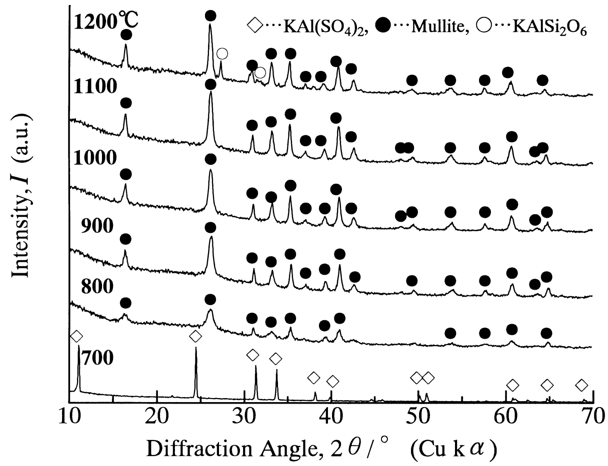

Fig. 3. XRD patterns of the samples obtained by heating the starting powder mixture containing 27.5 mol% of SiO_2 at 700–1200°C for 3 h and then treating with hot 1 N HCl.

that the lattice parameters did not change. In contrast, with increasing SiO_2 content, a halo peak of XRD, which corresponds to an amorphous form of SiO_2, became clear. The mullite crystal is considered to coexist with the amorphous SiO_2 under these experimental conditions. Although a small amount of amorphous SiO_2 seemed to be present, the starting powder mixture containing 27.5 mol% of SiO_2, namely the powder mixture consisting of 24.5 mol% of $Al_2(SO_4)_3$, 48.0 mol% of K_2SO_4 and 27.5 mol% of SiO_2, was found to be optimal for yielding mullite crystal and thus was selected for following experiments.

Fig. 3 shows XRD patterns of the samples obtained by heating the starting powder mixture containing

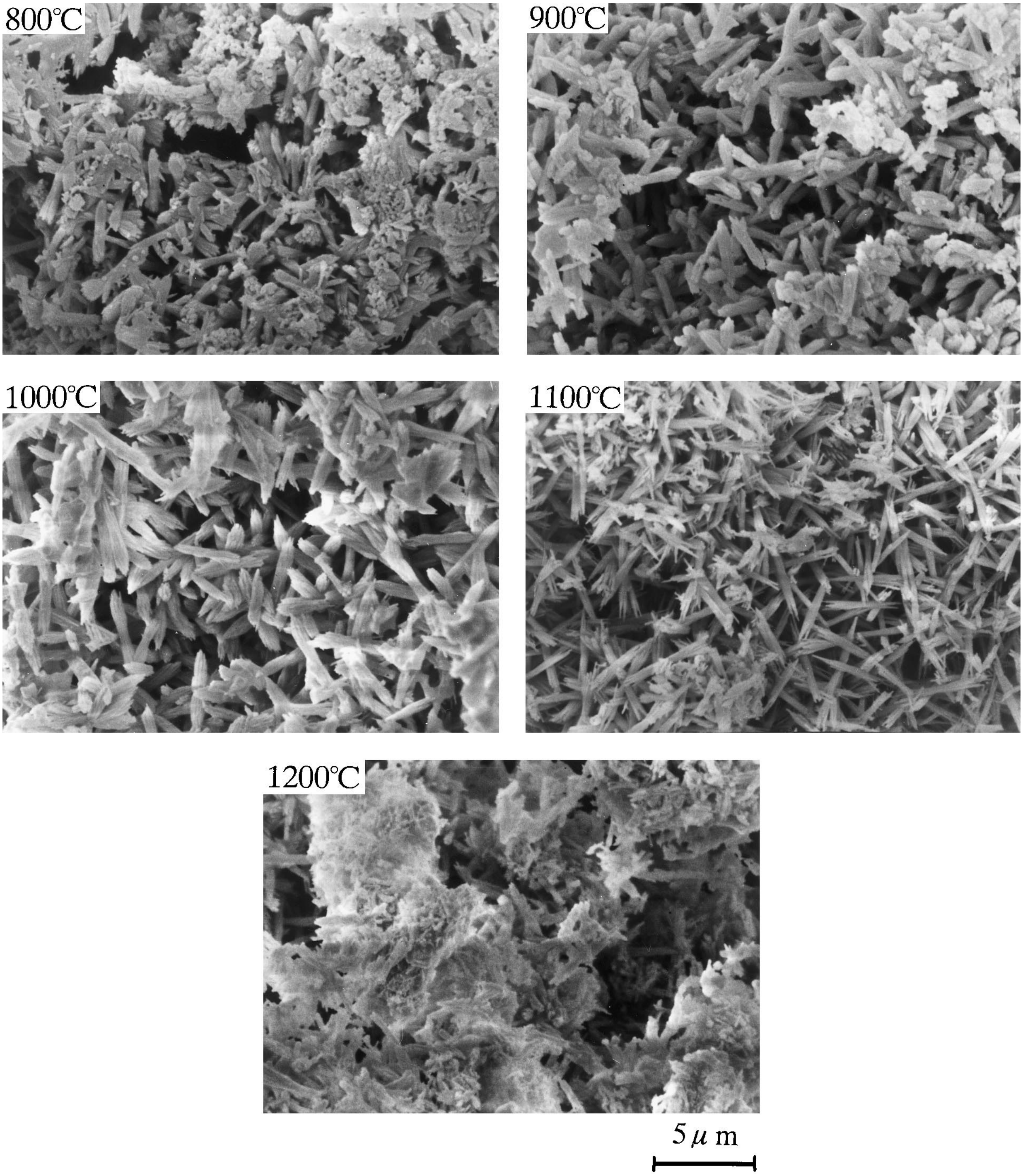

Fig. 4. SEM photographs of the samples obtained by heating the starting powder mixture containing 27.5 mol% of SiO_2 at 800–1200°C for 3 h and then treating with hot 1 N HCl.

27.5 mol% of SiO_2 at 700–1200°C. At the lowest heating temperature, 700°C, only $KAl(SO_4)_2$ crystalline phase was identified, and at the highest temperature, 1200°C, mullite and $KAlSi_2O_6$ crystalline phases were detected. The crystalline phase in the samples heated in the temperature range 800–1100°C were only mullite.

Fig. 4 shows SEM photographs of the samples obtained by heating the starting powder mixture containing 27.5 mol% of SiO_2 heated at 800–1200°C. When the sample was heated at 800°C, some of the mullite particles became needlelike. At 900°C, the particles were 2–3 μm in length and 0.5–1 μm in width. At 1000°C, the maximum length of the mullite particle was 4 μm, and both ends of the particle were observed to branch into fine needles. At 1100°C, the length of the particles was 2–5 μm, whereas the width decreased to 0.2–0.5 μm. At the ends of the needlelike particles, smaller needles were observed. With increasing heating temperature, the external morphology of the mullite particles changed to the needlelike form. At 1200°C, these needlelike mullite particles interlinked with each other, forming aggregated crystals. These aggregated crystals appear to have formed by the precipitation of $KAlSi_2O_6$ crystal.

Fig. 5 shows the specific surface area of the samples obtained by heating the starting powder mixture containing 27.5 mol% of SiO_2 at 800–1200°C. The specific surface area exhibited a tendency to increase with increasing heating temperature and the development of the needlelike mullite particles. At 1100°C, a maximum specific surface area of 136 m^2/g was obtained. At 1200°C, the formation of aggregated crystals without needlelike particles is thought to have decreased the specific surface area.

3.2. Formation process of mullite particles

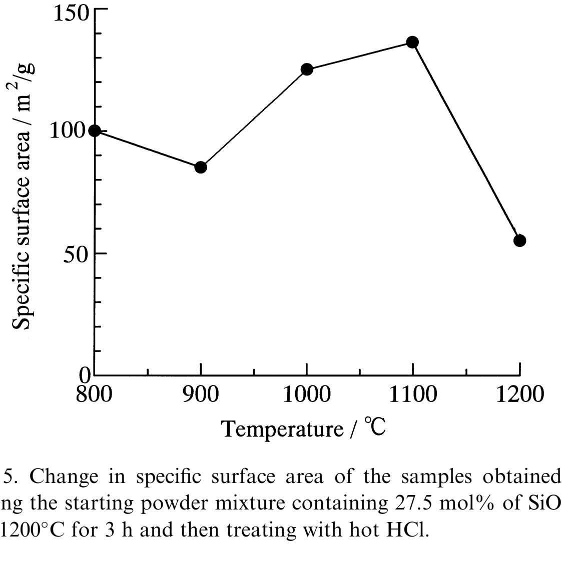

Fig. 5. Change in specific surface area of the samples obtained by heating the starting powder mixture containing 27.5 mol% of SiO_2 at 800–1200°C for 3 h and then treating with hot HCl.

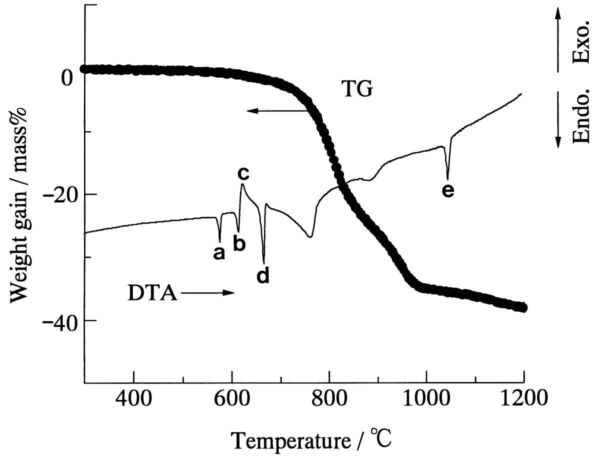

Fig. 6. DTA and TG curves of the starting powder mixture containing 27.5 mol% of SiO_2 heated up to 1200°C at a rate of 10°C/min.

Fig. 6 shows DTA and TG curves of the starting powder mixture containing 27.5 mol% of SiO_2. Four endothermic peaks: a (approx. 570°C), b (600°C), d (660°C) and e (1030°C) and one exothermic peak: c (620°C) were observed. Endothermic peak (a) is thought to be caused by the transformation β-phase (low-temperature form) to α-phase (high-temperature form) of K_2SO_4 (585°C).[14,15] The cause of the endothermic peak (b) is not clear. Fig. 7 shows XRD patterns of the samples obtained by heating the starting powder mixture containing 27.5 mol% of SiO_2 to temperatures of up to 600, 620, 660, and 1100°C, respectively, and then cooling rapidly to room temperature. When the sample was heated up to 620°C [exothermic peak (c)], the crystalline phase in the sample was identified as being primarily $K_3Al(SO_4)_3$. Accordingly, the exothermic peak (c) is thought to be caused by the formation of $K_3Al(SO_4)_3$ crystal. The endothermic peak (d) is thought to be due to the formation of a liquid phase,

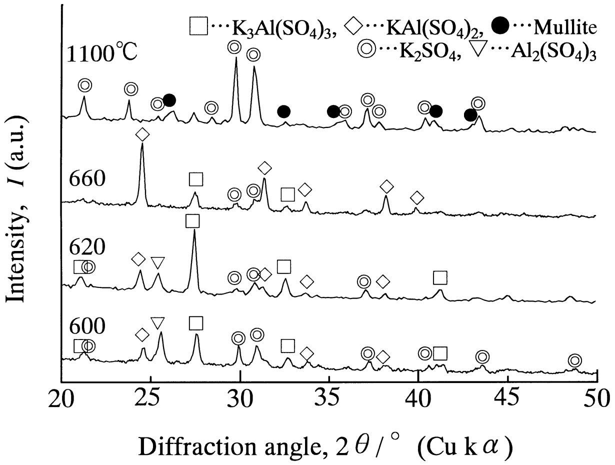

Fig. 7. XRD patterns of the samples obtained by heating the starting powder mixture containing 27.5% of SiO_2 heated temperatures of up to 600, 620, 660 and 1100°C, respectively, and then cooling rapidly to room temperature.

because the melting point of $K_3Al(SO_4)_3$ is 690°C.[16] After being heated to 660°C, the sample shrank remarkably and was identified as being primarily $KAl(SO_4)_2$ crystal, so that $KAl(SO_4)_2$ is thought to be formed from the liquid phase. $KAl(SO_4)_2$ has been reported to be thermodynamically stable up to approximately 727°C,[17] but its melting point and thermal stability are not clear. At 800°C, mullite crystal began to form, as shown in Fig. 3. Finally, the sample that was heated to 1100°C was identified as consisting of mullite and K_2SO_4 crystals, thus the $K_3Al(SO_4)_3$ and $KAl(SO_4)_2$ crystals seem to have disappeared.

Based on the above mentioned results, the formation process of the needlelike mullite particles is discussed as follows. Initially, $K_3Al(SO_4)_3$ is formed below 620°C in accordance with Eq. (1), as shown below. In this system, a liquid phase consisting of primarily $K_3Al(SO_4)_3$ is thought to be formed at approximately 660°C. Since the sample that was cooled rapidly from 660°C to room temperature was identified as being primarily $KAl(SO_4)_2$, the $K_3AI(SO_4)_3$ is thought to react with the remaining $Al_2(SO_4)_3$ to form $KAl(SO_4)_2$, in accordance with Eq. (2), as shown below. At temperatures above 800°C, mullite is thought to be primarily formed according to Eq. (3).

$$Al_2(SO_4)_3(s) + 3K_2SO_4(s) = 2K_3Al(SO_4)_3(s) \quad (1)$$

$$K_3Al(SO_4)_3(l) + Al_2(SO_4)_3(s) = 3KAl(SO_4)_2(s, l) \quad (2)$$

$$\begin{aligned} &6KAI(SO_4)_2(s, l) + 2SiO_2(s) \\ &= 3Al_2O_3 \cdot 2SiO_2(s) + 3K_2SO_4(s) + 9SO_3(g) \end{aligned} \quad (3)$$

The formed mullite particles become needlelike because they grow in coexistence with liquid phase in the sample. The remarkable weight decrease indicated by the TG curve from approximately 700 to 1000°C, as seen in Fig. 6, is thought to be due to the vaporization of $SO_3(g)$ based on Eq. (3). Therefore, the weight loss is in agreement with the calculated value of $SO_3(g)$ by the thermal decomposition of $Al_2(SO_4)_3$ (approximately 32%). A slight weight loss at temperatures above 1000°C may be due to vaporization of K_2SO_4. The melting point of K_2SO_4 is 1069°C,[14] so that endothermic peak (e) is thought to be caused by the melting of K_2SO_4 reformed by Eq. (3). At 1100°C, the amount of the

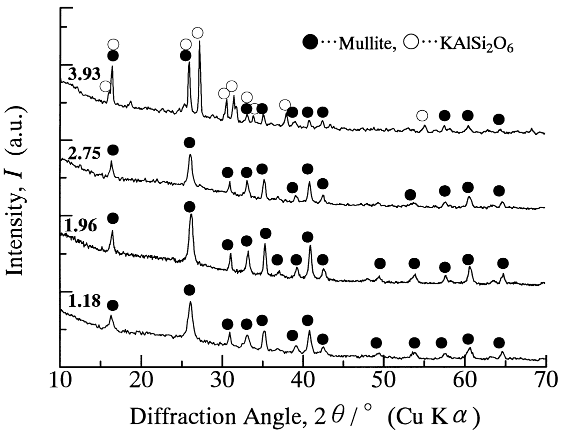

Fig. 8. XRD patterns of the samples obtained by heating the starting powder mixtures of [$Al(SO_4)$:SiO_2:K_2SO_4 = 1:1.12:X, (X = 1.18, 1.96, 2.75, 3.93)] at 1000°C for 3 h and then treating with hot HCI.

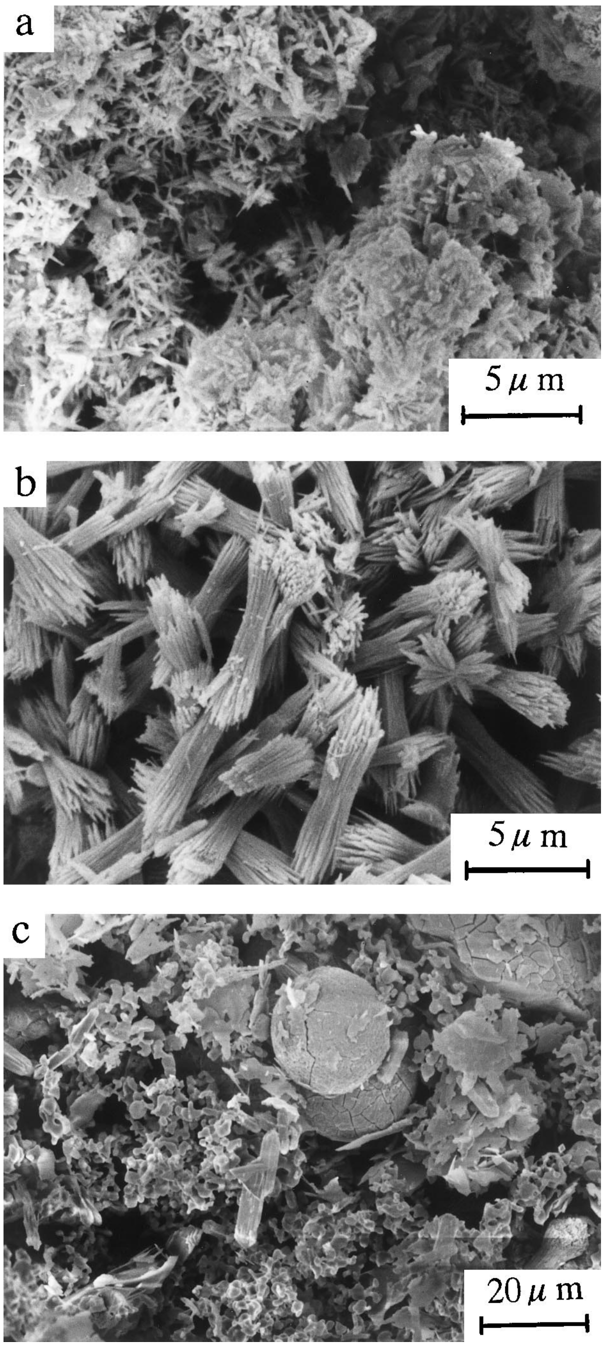

Fig. 9. SEM photographs of the samples obtained by heating the starting powder mixtures of [$Al_2(SO_4)$:SiO_2:K_2SO_4 = 1:1.12:X (mol%)], [((a) X = 1.18, (b) X = 2.75 and (c) X = 3.93)] at 1000°C for 3 h and then treating with hot HCl.

liquid phase is thought to be adequate for growing the needlelike mullite particles.

3.3. *Effect of the amount of K_2SO_4 flux*

The effect of the amount of K_2SO_4 flux on the formation of needlelike mullite particles was investigated. Fig. 8 shows XRD patterns of the samples obtained by heating the starting powder mixtures of [$Al_2(SO_4)$: SiO_2:K_2SO_4 = 1:1.12:X (mol%), (X = 1.18, 1.96, 2.75, 3.93)] at 1000°C. When $X = 1.18 \sim 2.75$, the crystalline phases in the samples were only mullite. When $X = 1.96$, the diffraction peaks of mullite became sharper than the other cases, namely $X = 1.18$ and 2.75, so that the crystallinity of the mullite is thought to be the best under these experimental conditions. When the sample having $X = 3.93$ was heated, the peak heights of mullite weakened, whereas the peak heights of $KAlSi_2O_6$ increased. A large amount of K_2SO_4 flux is not good for synthesizing mullite crystal. Fig. 9 shows SEM photographs of the samples obtained by heating the starting powder mixtures of [$Al_2(SO_4)$:SiO_2:K_2SO_4 = 1:1.12:X(mol%), ((a):$X = 1.18$, (b): $X = 2.75$, and (c) $X = 3.93$)] at 1000°C. For comparision, Fig. 4 shows SEM photograph for $X = 1.96$ (1000°C). The SEM photograph for $X = 1.18$ shows the formation of fine needlelike particles of approximately 1 μm in length. However, several aggregated crystals were also formed. In contrast, at $X = 2.75$, the amount of K_2SO_4 flux was still adequate for growing the needlelike mullite particles. As shown in Fig. 9(b), these particles reached a length of approximately 8 μm and a width of 1–2 μm. Furthermore, the particle branched into small needlelike particles at both ends. In contrast, at $X = 3.93$, most of the particles were spherical or irregular in form. These particles are thought to be $KAlSi_2O_6$ crystal. Needelike particles were not observed.

Judging from these results, fine and long needlelike mullite particles appear to have been obtained by heating the powder mixture consisting of $Al_2(SO_4)$:K_2SO_4:-SiO_2 = 24.5: 48.0: 27.5 (mol%) at 1100°C.

4. Summary

Needlelike mullite particles were obtained by heating a powder mixture consisting of $Al_2(SO_4)_3$, SiO_2 and K_2SO_4 in an alumina crucible covered with a lid. When the powder mixture consisting of 24.5 mol% of $Al_2(SO_4)_3$, 48.0 mol% of K_2SO_4 and 27.5 mol% of SiO_2 was heated at 1100°C for 3 h, fine and long mullite particles were obtained. The particles were 0.2–0.5 μm in width and 2–5 μm in length. The specific surface area of these mullite particles was 136 m^2/g.

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