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Formation of Porous Aggregations Composed of Al_2O_3 Platelets Using Potassium Sulfate Flux

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Abstract

Porous aggregations, with about 10 μm diameter, composed of Al_2O_3 platelet crystals were formed by heating a powder mixture consisting of $Al_2(SO_4)_3 + 2K_2SO_4$ (mol ratio) in an alumina crucible at temperatures 1000–1300°C for 3 h and removing the flux component with hot hydrochloric acid after heating. The specific surface area of the aggregations obtained by heating at 1000°C for 3 h was maximum and its value was 5·2 $m^2 g^{-1}$. Since the size of Al_2O_3 platelets increased and the number of Al_2O_3 platelets decreased, the specific surface area decreased to 0·7 $m^2 g^{-1}$ at 1100°C. When heated at 1300°C, the size of the Al_2O_3 platelets increased with increasing amount of K_2SO_4 in the starting powder mixture.

Keywords: flux growth, platelets, Al_2O_3, microstructure – final, surfaces.

1 Introduction

Highly developed anisotropic ceramic particles, for example whiskers and platelets, are used as reinforcements of metal or ceramics to improve their mechanical properties such as elastic modulus, toughness and strength. The use of ceramic whiskers, however, causes difficulties of processing. On the other hand, ceramic platelets are easy to disperse into a matrix phase, and their use has recently increased. Al_2O_3 platelets have been grown by hydrothermal reaction[1] and in different kinds of fluoride flux.[2,3] Different matrices for example mullite,[4] sialon,[5] aluminium-based metal matrix,[6] glass,[7] ($Ce–ZrO_2 + Al_2O_3$)[8] and TiO_2[9] reinforced by Al_2O_3 platelets have shown remarkable improvements of the mechanical properties as compared with the unreinforced matrices.

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As a basic research on the formation of porous aggregations composed of Al_2O_3 platelets with high potential capacity, we have studied the Al_2O_3 products which are grown by heating $Al_2(SO_4)_3$ in a K_2SO_4 flux. The aim of this study is to determine the formation temperature of the porous aggregations composed of Al_2O_3 platelet crystals in the case of heating $Al_2(SO_4)_3$ in K_2SO_4 flux, to observe the morphology of the Al_2O_3 and to examine the specific surface area of the Al_2O_3. The growth mechanism of the Al_2O_3 is also discussed.

2 Experimental Procedure

As starting materials, $Al_2(SO_4)_3 \cdot 14–18H_2O$ and K_2SO_4 of reagent-grade were used. The $Al_2(SO_4)3 \cdot 14–18H_2O$ was preheated at 300°C for 12 h to form $Al_2(SO_4)_3$, the formation of which was confirmed by X-ray diffractometry (XRD) analysis. Each powder mixture (about 10 g) consisting of $Al_2(SO_4)_3/K_2SO_4 = 1/1$, 1/2 and 1/3 (mol ratio) was put into an alumina crucible (60 mm diameter, 75 mm high) covered by an alumina lid and then heated at temperatures in the range 800–1500°C for 3 h. The heating and cooling rates of the furnace were 10°C min^{-1}. After the heat treatment, a mass remained at the bottom of the alumina crucible. The mass was treated with 70–80°C, 1 N hydrochloric acid for 0·5–1 h. White powders were obtained as final products. The powders were analyzed by XRD to identify the crystal phases and the particle morphology of the powders was observed by scanning electron microscopy (SEM). The specific surface area of the powders was examined by the BET method. To elucidate the growth mechanism of this Al_2O_3, differential thermal analysis (DTA) and thermogravimetric analysis (TG) for the starting powder mixture were performed up to 800°C with a heating rate of 10°C min^{-1}.

3 Results and discussion

3.1 Formation

Figure 1 shows XRD patterns of the final powders after heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at various temperatures for 3 h and treating with hot hydrochloric acid. As heated at 800°C, the powder was identified as $KAl(SO_4)_2$ crystals. Al_2O_3 crystals were first detected after heating at temperatures above 900°C, but the peaks of β-Al_2O_3 (KAl_5O_8 and $K_2Al_{22}O_{34}$ crystals) were detected in addition at 1400°C. In the case of heating at 1500°C, the intensities of the main peaks corresponded to β-Al_2O_3 (KAl_5O_8 and $K_2Al_{22}O_{34}$) and the Al_2O_3 signal was very low. That is to say, Al_2O_3 powder as a simple crystal phase was obtained at temperatures between 900 and 1300°C. Figure 2 shows SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 900°C. As a whole, the shape of the Al_2O_3 is inhomogeneous. However, nearly spherical aggregations with less than 10 μm diameter could be observed. The surfaces of the aggregations were rough. Figure 3 shows SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 1000°C. Most of the Al_2O_3 comprised nearly spherical porous aggregations, of about 10 μm, composed of small platelet crystals. The size of the Al_2O_3 platelet crystals which appeared at the surface of the aggregations was 0·2 to 0·4 μm short side and 1 to 2 μm long side.

3.2 Changes of morphology and specific surface area

Figure 4 shows the specific surface area of Al_2O_3 powders prepared by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at temperatures between 900 and 1300°C. The maximum was obtained at

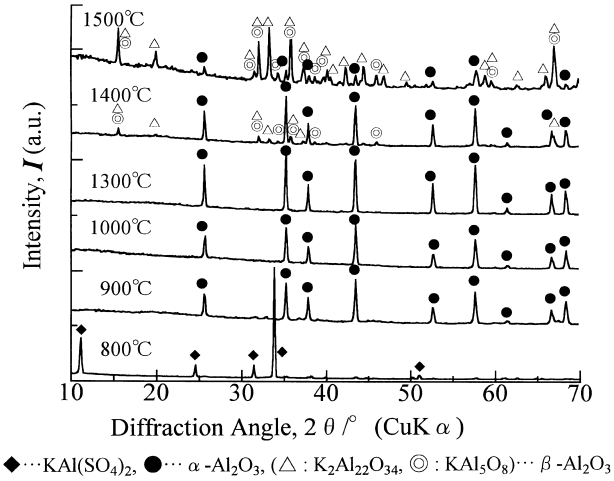

Fig. 1. XRD patterns of the final powders after heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at various temperatures for 3 h and treating with hot hydrochloric acid.

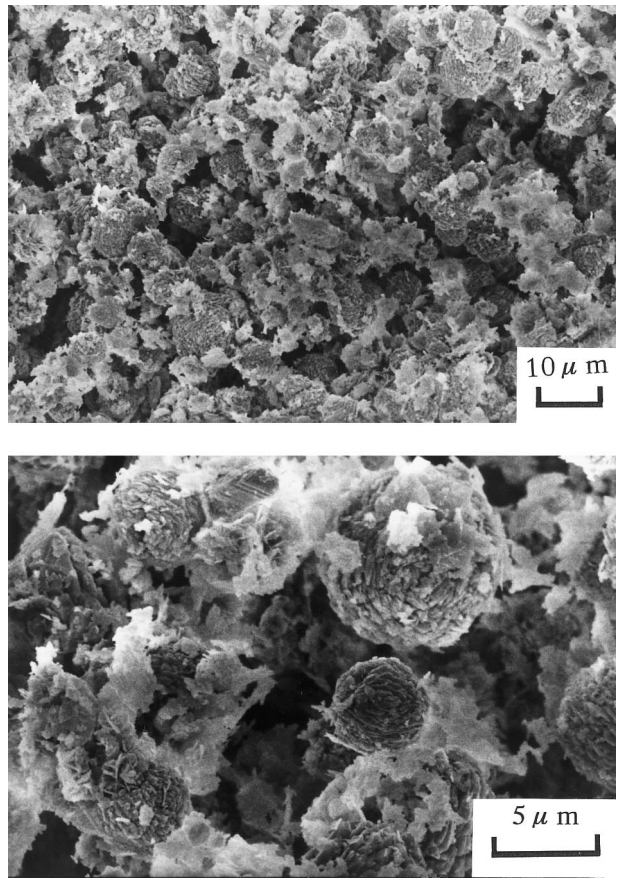

Fig. 2. SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 900°C for 3 h.

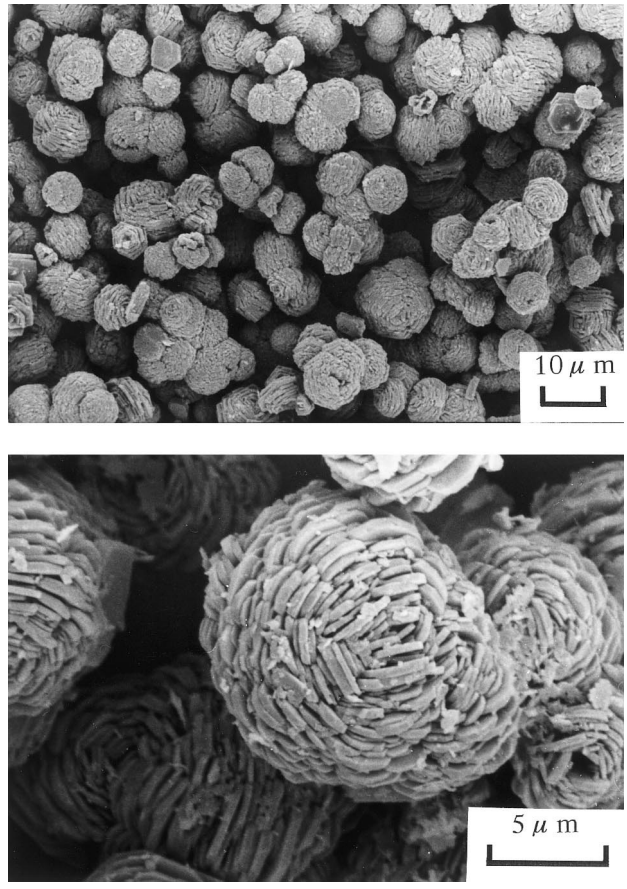

Fig. 3. SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 1000°C for 3 h.

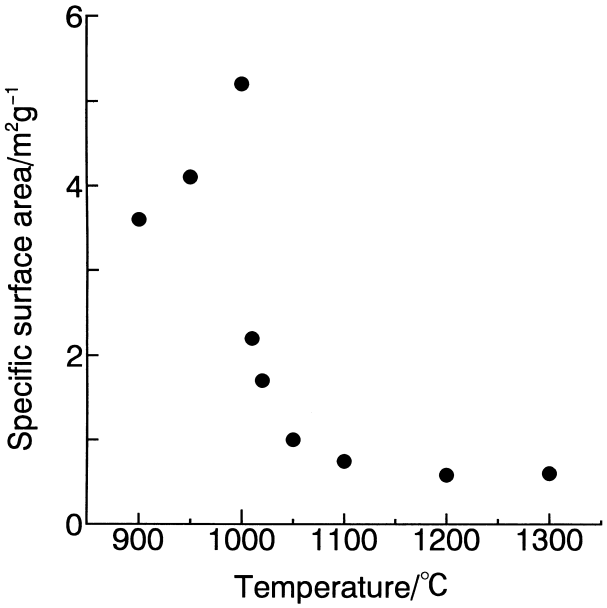

Fig. 4. Specific surface area of Al_2O_3 powders prepared by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at temperatures between 900–1300°C for 3 h.

1000°C and its value was $5{\cdot}2\,m^2\,g^{-1}$. The specific surface area then decreased to $0{\cdot}7\,m^2\,g^{-1}$ at 1100°C, keeping almost the same value to 1300°C. Figure 5 shows SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 1300°C. Porous aggregations composed of Al_2O_3 platelets were again observed. The size of the aggregations was about 10 μm diameter and similar to those shown in Fig. 3. However, the size of the Al_2O_3 platelets increased, while the number of platelets decreased. In appearance, the short side and long side of the Al_2O_3 platelets near the surface of the aggregations were 0·5 to 1 μm and several μm to 10 μm, respectively. According to SEM observation, the size and morphology of the aggregations composed of Al_2O_3 platelets obtained by heating at temperatures 1100–1200°C were similar to those of the aggregations obtained by heating at 1300°C, seen in Fig. 5.

3.3 Growth mechanism

Figure 6 shows TG and DTA curves for the starting powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ up to 800°C. The melting point of K_2SO_4 is 1069°C.[10] $Al_2(SO_4)_3$ is desulfurized in air at above 900°C to form Al_2O_3.[11] Two endothermic peaks and one exothermic peak were detected at about 580°C (point a), 660°C (point c) and 620°C (point b), respectively. The first endothermic peak (a) is considered to be caused by the transformation from the β-(low temperature form) to the α-phase (high temperature form) of K_2SO_4.[10,12] The powder mixture which was heated to 640°C and then cooled rapidly to room temperature resembled the

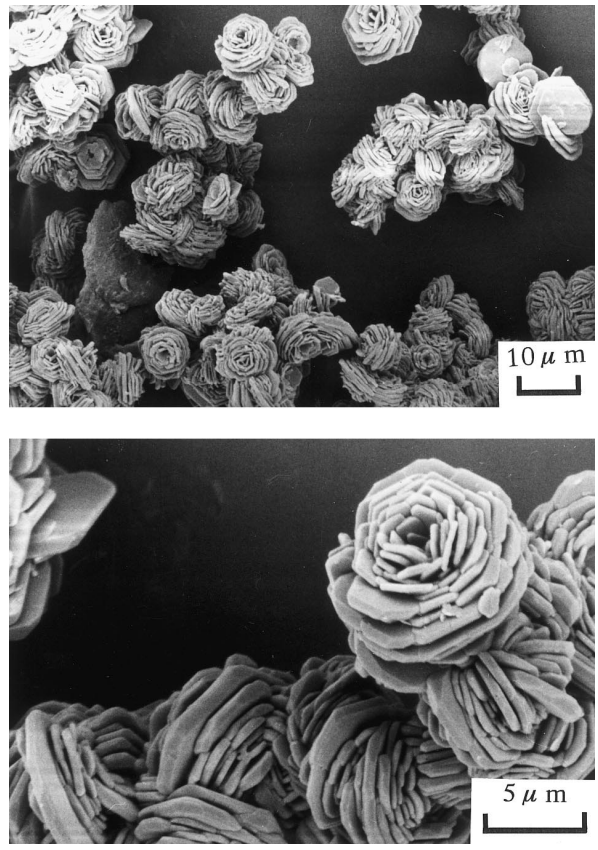

Fig. 5. SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 1300°C for 3 h.

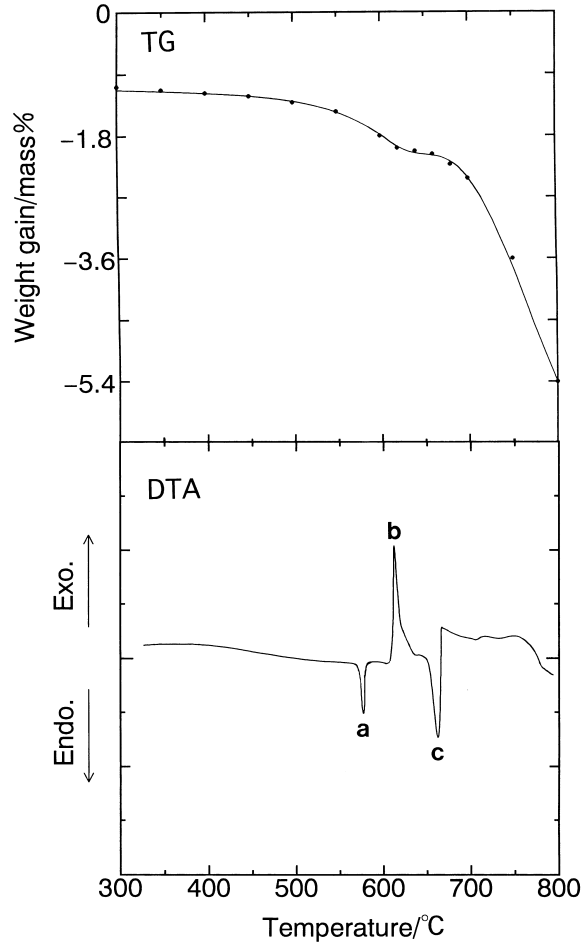

Fig. 6. TG and DTA curves for the starting powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ up to 800°C.

starting powder mixture and was mostly identified as $K_3Al(SO_4)_3$ crystals, although low intensity peaks corresponding to $KAl(SO_4)_2$ and $Al_2(SO_4)_3$ were detected. Therefore, the exothermic (b) is considered to be caused by the formation of $K_3Al(SO_4)_3$ crystal. Since after the DTA cycle (heated up to 800°C) of the starting powder mixture, no individual particles could be distinguished and luster was observed in some places, the second endothermic peak (c) is considered to be due to the formation of a liquid phase.

The reason why the final powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 800°C for 3 h was identified as $KAl(SO_4)_2$ crystal, as seen in Fig. 1, is that the composition of the liquid changed by the vaporization of SO_3 (g) with heating, which was noticed in the TG curve of Fig. 6; the $KAl(SO_4)_2$ finally crystallized from the liquid during cooling.

According to SEM observation of the Al_2O_3 powder obtained by rapid cooling to room temperature after heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$ at 1000°C for 3 h, the size and morphology of the porous aggregations of Al_2O_3 platelets were almost the same as those cooled at 10°C min^{-1}, seen in Fig. 3. The aggregations composed of Al_2O_3 platelets are considered to be grown in the liquid phase during heating.

Since the change of Gibbs' free energy ($\Delta G°$) for the following equation at 827°C (1100 K) is -1442.114 kJ mol^{-1}, based on thermochemical data,[10] it is expected that nucleation is caused and that stable Al_2O_3 crystals precipitate in the liquid phase.

$$Al_2(SO_4)_3 + 3K_2O = 3K_2SO_4 + Al_2O_3$$

With increasing temperature, it is considered that the vaporization of SO_3 (g) from the liquid is accelerated to form Al_2O_3 crystal. As shown in Fig. 7 which shows the formation process of the porous aggregations of Al_2O_3 platelets, during the second stage, multinucleation of Al_2O_3 crystals may occur at the surface of the original Al_2O_3 crystal. They will grow to form the aggregation of Al_2O_3 platelets.

Figures 8 and 9 show SEM photographs of Al_2O_3 powder obtained by heating the powder mixtures of $Al_2(SO_4)_3/K_2SO_4 = 1/1$ and 1/3 at 1300°C for 3 h, respectively. In the case of heating the powder mixture of 1/1, Al_2O_3 platelets

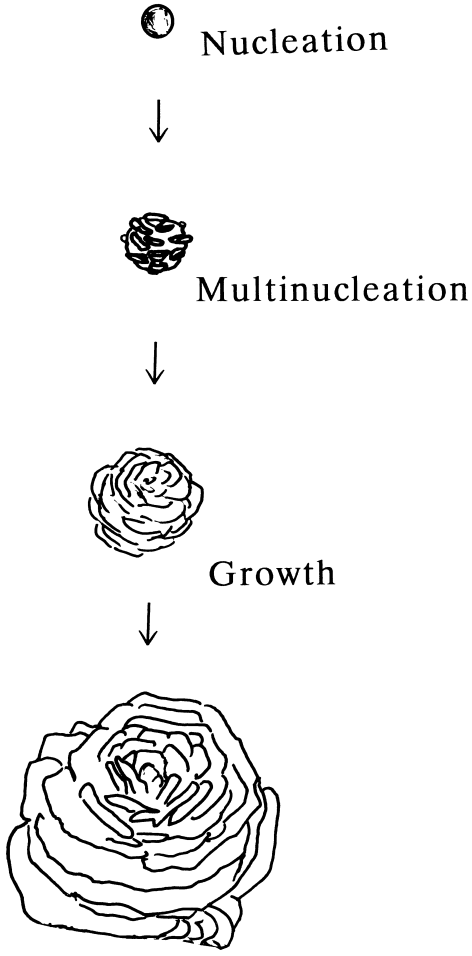

Fig. 7. Schematic drawing for the formation process of the porous aggregations of Al_2O_3 platelets.

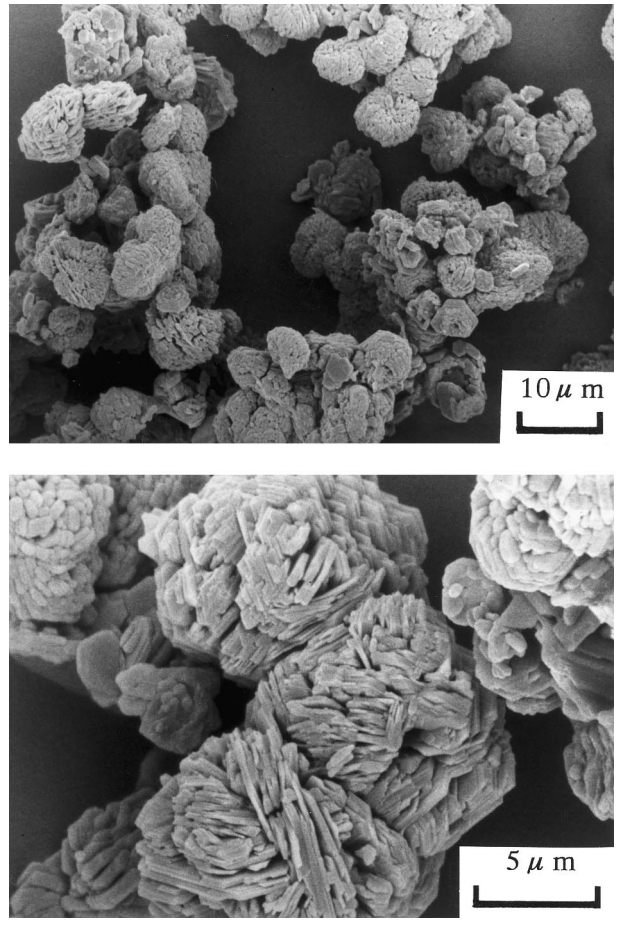

Fig. 8. SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/1$ at 1300°C for 3 h.

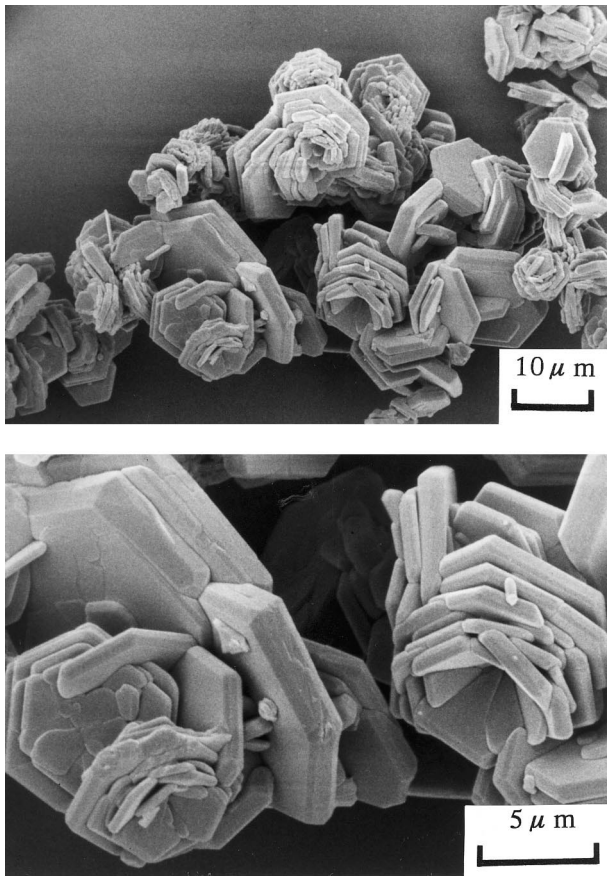

Fig. 9. SEM photographs of Al_2O_3 powder obtained by heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/3$ at 1300°C for 3 h.

appeared to be interlinked to each other due to shortage of the liquid phase during heating. On the other hand, with heating the powder mixture of 1/3, Al_2O_3 platelets grew. The amount of the liquid phase is considered to be enough for the Al_2O_3 platelets to develop. K_2SO_4 is considered to take an important part as the flux component in this method.

4 Conclusions

To form porous aggregations composed of Al_2O_3 platelets, powder mixture consisting of $Al_2(SO_4)_3$ and K_2SO_4 were heated at temperatures between 800 and 1500°C and treated with hot hydrochloric acid to remove the flux component after heating. The major results are as follows.

1. On heating the powder mixture of $Al_2(SO_4)_3/K_2SO_4 = 1/2$, porous aggregations, of about 10 μm diameter, composed of α-Al_2O_3 platelet crystals were obtained by heating at temperatures 1000–1300°C. As heated at temperatures 1100–1300°C, the size of the Al_2O_3 platelets increased and the number of Al_2O_3 platelets decreased, as compared with those formed at 1000°C.

   The specific surface area of the aggregations composed of Al_2O_3 platelets reached $5{\cdot}2\,m^2\,g^{-1}$ at 1000°C, it then decreased to $0{\cdot}7\,m^2\,g^{-1}$ at 1100°C and was almost constant for temperatures 1100–1300°C.
2. In the case of heating at 1300°C, the size of the Al_2O_3 platelets increased with increasing K_2SO_4 in the starting powder mixture.

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