Synthesis of Needlelike Leucite Crystals Using Potassium Sulfate Flux

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硫酸カリウムフラックスを用いた針状リュースイト結晶の合成

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When a powder mixture consisting of $\text{Al}_2(\text{SO}_4)_3$, SiO_2 and K_2SO_4 was heated in a closed alumina crucible, a reactant mass remained at the bottom of the crucible. Needlelike leucite crystals were obtained by treating this reactant mass with hot HCl. The effect of the mixing ratio of the raw materials, the heating temperature and the duration of heating at the selected temperature on the formation of needlelike leucite crystals was investigated. When a powder mixture, consisting of $\text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 : \text{K}_2\text{SO}_4 = 1.0 : 2.8 : 1.9$ (molar ratio), was heated at 1200°C for 3 h, the obtained needlelike leucite crystals were $1\text{--}2\ \mu\text{m}$ in length and $0.1\text{--}0.3\ \mu\text{m}$ in width. Needlelike leucite crystals were formed by the crystallization of leucite on small mullite crystals obtained by heating, followed by growth of the leucite crystals in a liquid phase of the K_2SO_4 flux as the main component.

[Received January 13, 2000; Accepted May 24, 2000]

Key-words: Synthesis, Needlelike leucite crystals, Potassium sulfate flux, Formation mechanism

1. Introduction

KAlSi_2O_6 (leucite) ceramics have been used as a reinforcement for dental porcelain or dental glass materials due to their tone and color appeal and excellent biocompatibility.^{(1)–(3)} The melting point of leucite is 1693°C ⁽⁴⁾ and its thermal expansion coefficient is high;^{(2), (5)} the expansivity is similar to those of metals such as copper and aluminum, so that the use of leucite as a reinforcement or coatings for their metal materials is also expected.⁽⁶⁾ However, while leucite ceramics are expected to be used as a reinforcement, leucite particles that grow in a fixed crystallographical direction to form whiskers, needlelike crystals or platelets have not yet been synthesized.

In the present study, a method for synthesizing needlelike leucite crystals using K_2SO_4 flux was investigated in order to use them as a reinforcement for dental ceramics or metal materials. Powder mixtures of $\text{Al}_2(\text{SO}_4)_3$, SiO_2 and K_2SO_4 were heated in air for the synthesis of needlelike leucite crystals. The effects of the mixing ratios of the raw materials, the heating temperature and the duration of heating at the selected temperature on the formation of needlelike leucite crystals were investigated. Furthermore, the formation mechanism of needlelike leucite crystals was discussed based on the morphological change of the starting powder mixture during heating.

2. Experimental procedure

As raw materials, $\text{Al}_2(\text{SO}_4)_3$ 14–18H₂O, SiO_2 and K_2SO_4 of reagent grade were used. Before the experiments were performed, $\text{Al}_2(\text{SO}_4)_3$ 14–18H₂O was heated at 300°C for more than 12 h to change it to $\text{Al}_2(\text{SO}_4)_3$ completely. SiO_2 was in the form of flakelike amorphous particles (mean particle size: $10\ \mu\text{m}$) with high reactivity. Starting powder mixtures were prepared by mixing $\text{Al}_2(\text{SO}_4)_3$, SiO_2 and K_2SO_4 in various ratios with acetone and drying them. Each of the starting powder mixtures (approximately 20 g) was placed in an alumina crucible (70 mm in height, 50 mm in diameter) and was covered with a lid. Each crucible was set in an electric furnace, heated at $1000\text{--}1250^\circ\text{C}$ at a rate of $10^\circ\text{C}/\text{min}$ and then maintained for various times at the selected temperature. After heating, the electric power of the furnace was switched off and the crucible was allowed to cool naturally in the furnace to room temperature. A reactant

mass, which remained at the bottom of the crucible after heating, was soaked in 3% HCl at $70\text{--}80^\circ\text{C}$ for 0.5–1 h to dissolve the K_2SO_4 flux, washed with water and dried well to obtain white particles as the final product. The crystalline phase of the particles was examined by X-ray diffraction (XRD) analysis. In order to compare the crystallinity of the particles, XRD examination was performed under the same conditions for all experiments. Furthermore, the micromorphology of the particles was observed by scanning electron microscopy (SEM). In order to elucidate the mechanism underlying the formation of needlelike leucite crystals, differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed for the starting powder mixture of $\text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 : \text{K}_2\text{SO}_4 = 1.0 : 2.8 : 1.9$ (molar ratio) which was heated at 1200°C at a rate of $10^\circ\text{C}/\text{min}$ and maintained for 3 h at that temperature in air.

3. Results

3.1 Formation of needlelike leucite crystals

Figure 1 shows the states of samples after heating the powder mixtures with various compositions at 1200°C for 3 h, and XRD patterns of the selected samples (indicated by a, b, c). In Fig. 1, dots denote the compositions that yielded the crystalline phase of only leucite. Triangles denote the compositions that yielded the crystalline phases of leucite and mullite. Since the diffraction peak intensities indicating mullite were relatively weak, the amount of the crystalline phase of mullite was concluded to be small. In contrast, squares denote the compositions that yielded reactant masses that were insoluble in hot HCl even after immersion for more than 1 h. The crystalline phase of the selected sample, indicated by c in Fig. 1, was only leucite. As an example of morphological observation, the starting powder mixture consisting of $\text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 : \text{K}_2\text{SO}_4 = 1.0 : 2.8 : 1.9$ that yielded only leucite crystal was selected. Figure 2 shows SEM micrographs of this sample. The sample was composed of porous grains $10\text{--}20\ \mu\text{m}$ in diameter, the largest grain being approximately $40\ \mu\text{m}$ in diameter. Upon further detailed observation of the grains, it was found that one grain is composed of fine needlelike particles $1\text{--}2\ \mu\text{m}$ in length and $0.1\text{--}0.3\ \mu\text{m}$ in width. Most of the other grains were also composed of fine needlelike particles. The diffraction peaks were identified to be those of leucite; thus, the

Fig. 1. States of samples after heating starting powder mixtures with various compositions at 1200°C for 3 h and then treating them with hot HCl, and XRD patterns of the selected samples (indicated by a, b, c in the composition triangle).

needlelike particles were confirmed to be leucite crystal. When SEM observation was performed for samples of other compositions as indicated by dots, the starting mixture consisting of $\text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 : \text{K}_2\text{SO}_4 = 1.0 : 2.8 : 1.9$ was found to be optimal for yielding needlelike leucite crystals and thus was used in the following experiments.

3.2 Effect of heating temperature

Figure 3 shows XRD patterns of samples obtained by heating the starting powder mixture at 1000–1250°C for 3 h. At the lowest temperature of 1000°C, the crystalline phase of the sample consisted of only mullite. The crystallinity and amount of mullite were found to be low and small, based on the broad diffraction peaks and their weak intensities, respectively. At 1100°C, both mullite and leucite existed in the sample. In both crystals, the diffraction peaks were weak; therefore, the amounts of these crystals were small. At 1150–1250°C, most of the diffraction peaks were identified to be those of leucite. The crystallinity of leucite was found to be high, based on the sharp diffraction peaks with strong intensities.

Figure 4 shows SEM micrographs of leucite crystals obtained by heating the starting powder mixtures at 1150 and 1250°C for 3 h. At 1150°C, needlelike particles similar to those in Fig. 2 were not observed, but some particles exhibited a needlelike shape of less than 1 μm in length. Aggregates of fine particles were also observed. At 1250°C, the micromorphology of the leucite crystal was similar to that obtained by heating at 1150°C. Therefore, the heating temperature is considered to have an important effect on the formation of needlelike leucite crystals, and the optimal heating temperature is estimated to be 1200°C.

Fig. 2. SEM micrographs of sample that was obtained by heating the starting powder mixture consisting of $\text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 : \text{K}_2\text{SO}_4 = 1.0 : 2.8 : 1.9$ at 1200°C for 3 h and then treating it with hot HCl.

Fig. 3. XRD patterns of samples obtained by heating the starting powder mixture at 1000–1250°C for 3 h and then treating it with hot HCl.

3.3 Effect of heating duration

The effect of heating duration on the crystalline phases and the micromorphology of the starting powder mixture that was heated at 1200°C was investigated. Figure 5 shows XRD patterns of samples obtained by heating the starting powder mixture at 1200°C for 0–2 h. As the crystalline phase, only mullite existed in the sample that was heated at 1200°C and then cooled rapidly to room temperature. However, the diffraction peaks representative of mullite were broad and their intensities were weak; thus, the crystallinity and amount of mullite were low and small, respectively. Mullite and leucite existed in the sample that was heated at 1200°C for 0.5 h, but both crystals were considered to have low crystallinity and small amount for the same reasons as mentioned above. When the starting powder mix-

Fig. 4. SEM micrographs of samples obtained by heating the starting powder mixture at 1150 and 1250°C for 3 h and then treating it with hot HCl.

Fig. 6. SEM micrographs of samples obtained by heating the starting powder mixture at 1200°C, cooling it rapidly to room temperature and then treating it with hot HCl.

Fig. 5. XRD patterns of samples obtained by heating the starting powder mixture at 1200°C for 0–2 h and then treating it with hot HCl.

ture was heated at 1200°C for 1 h, most of the diffraction peaks of the sample were identified to be those of leucite. The crystallinity of leucite was found to be high, based on the sharp diffraction peaks with strong intensities. Only leucite with high crystallinity existed in the samples that were heated at 1200°C for 1.5 and 2 h. Figure 6 shows SEM micrographs of samples obtained by heating the starting powder mixture at 1200°C and then cooling it rapidly to room temperature. The crystalline phase of the samples consisted of only mullite with low crystallinity. The sample was composed of grains 10–40 μm in diameter. Upon further detailed observation of the grains, it was found that most of the grains were composed of fine needlelike particles, similar to those shown in Fig. 2. The size of the needlelike particles was slightly less than that of needlelike leucite

crystal. The needlelike particles were also observed in all the samples that were obtained by heating at 1200°C for more than 0.5 h.

3.4 Behavior of the starting powder mixture during heating

Figure 7 shows TG and DTA curves of the starting powder mixture. Figure 8 shows XRD patterns of the starting powder mixture that was heated at 600, 820, 1000 and 1100 °C, cooled rapidly to room temperature and not treated with hot HCl. These temperatures are indicated in the DTA curve. In the DTA curve, three endothermic peaks (590, 790 and 1070°C) are observed. The sample that was heated at 600°C consisted of K_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$, and the sample that was heated at 820°C consisted of K_2SO_4 and $\text{K}_3\text{Al}(\text{SO}_4)_3$ crystals. Above 820°C, the peaks representative of the $\text{Al}_2(\text{SO}_4)_3$ crystal disappeared from the XRD patterns. The diffraction peaks of both samples that were heated at 1000 and 1100°C were identified as being those of only K_2SO_4 crystal. In the TG curve, the weight of the starting powder mixture began to decrease rapidly above 700°C and the weight loss reached approximately 30 mass% at 1000°C. At temperatures higher than 1000°C, the weight of the starting powder mixture continued to decrease gradually. Finally, the weight loss reached 37.3 mass% after being maintained for 3 h at 1200°C. In contrast, the weight loss of K_2SO_4 during heating was slight and reached 2.5 mass% after being maintained for 3 h at 1200°C.

4. Discussion

4.1 Behavior of the starting powder mixture during heating

First, the causes of the three endothermic peaks (590, 790 and 1070°C) in the DTA curve shown in Fig. 7 are discussed. The endothermic peak at 590°C is caused by the transformation of K_2SO_4 (585°C),⁷⁾ that is, the β -phase (low-temperature form) to the α -phase (high-temperature

Fig. 7. TG and DTA curves of the starting powder mixture.

Fig. 8. XRD patterns of the starting powder mixture that was heated at 600, 820, 1000 and 1100°C and then rapidly cooled to room temperature.

form). The sample that was heated at 820°C consisted of $K_3Al(SO_4)_3$ and K_2SO_4 . The melting point of $K_3Al(SO_4)_3$ is reported to be 690°C.⁸⁾ Therefore, it is estimated that a eutectic reaction occurred among $Al_2(SO_4)_3$, SiO_2 and K_2SO_4 . The endothermic peak at 790°C, namely, from 700 to 800°C, is thought to be caused by the formation of a liquid phase. $K_3Al(SO_4)_3$ precipitated from the liquid phase during the cooling process. The endothermic peak at 1070°C is caused by the melting of the K_2SO_4 flux that remained in the sample, because the melting point of K_2SO_4 is 1069°C.⁹⁾

The mass loss of the starting powder mixture during heating is discussed as follows. The drastic mass loss from approximately 700 to 1000°C (approximately 30 mass%) is in agreement with the mass ratio of $SO_3(g)$ decomposed from $Al_2(SO_4)_3$ for the total mass of the starting powder mixture (29.0 mass%). Therefore, the mass loss is caused by the evaporation of $SO_3(g)$ based on the following equation:

The cause of the endothermic reaction above 700°C in the DTA curve includes this decomposition reaction.

As shown in Fig. 8, the sample that was heated at 1000°C and then cooled rapidly to room temperature was identified

as being only K_2SO_4 . The Al_2O_3 that was generated according to Eq. (1) is thought to react rapidly with the raw materials to form mullite with low crystallinity and an amorphous phase. In fact, the broad diffraction peaks with weak intensities, which are indicative of mullite, and a halo peak at 20–25° of 2θ , which is indicative of an amorphous phase, were detected for the sample heated at 1000°C for 3 h.

4.2 Formation mechanism of needlelike leucite crystals

As shown in Fig. 5, when the starting powder mixture that was heated at 1200°C but not maintained at this temperature and cooled rapidly to room temperature was analyzed by XRD, broad diffraction peaks with weak intensities, which are indicative of mullite, and a halo peak at 20–25° of 2θ , which is indicative of an amorphous phase, were detected. However, the amount the mullite crystal is relatively small and its size is smaller than that of leucite crystals, based on the broad diffraction peaks representative of mullite. The sample exhibited needlelike particles (see Fig. 6), and the size and morphology of the particles were similar to those of needlelike leucite crystals (see Fig. 2). On the basis of the above results, the needlelike particles produced at 1200°C for 0 h are thought to form via the precipitation of leucite with low crystallinity (almost amorphous phase) on small mullite crystals during the cooling process. When the starting powder mixture was heated at 1200°C for longer durations, leucite crystals began to form in the sample. At the first step, the crystallization of leucite takes place according to the following equation. Therefore, the small mullite crystals are thought to play an important role as nuclei for the crystallization of leucite.

Subsequently, the growth of leucite crystals proceeds in the liquid phase of the K_2SO_4 flux as the main component to form needlelike leucite particles. In the TG curve shown in Fig. 7, the slight mass loss of the starting powder mixture while it is maintained at 1200°C is considered to be caused by the evaporation of $SO_3(g)$ from K_2SO_4 due to the further crystallization of leucite.

5. Conclusions

When a powder mixture consisting of $Al_2(SO_4)_3 : SiO_2 : K_2SO_4 = 1.0 : 2.8 : 1.9$ (molar ratio) is heated at 1200°C for 3 h and the formed reactant mass is treated with hot HCl, 10–20 μm porous aggregates of needlelike leucite crystals 1–2 μm in length and 0.1–0.3 μm in width are obtained. First, leucite crystals are formed by the reaction among small mullite crystals that initially form during the heating, SiO_2 and K_2SO_4 of the raw materials. Then, the growth of leucite crystals proceeds in the liquid phase of the K_2SO_4 flux as the main component to form needlelike crystals.

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