Synthesis of Spherical Leucite Crystals

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球状リューサイト結晶の合成

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When a powder mixture of K_2SO_4 , $Al_2(SO_4)_3$, and SiO_2 is heated at 1000°C in an alumina crucible covered with a lid, a solid phase remains at the bottom of the crucible. Spherical leucite crystals are obtained by treating this solid phase with hot HCl. The effects of the mixing ratio of the raw materials, heating temperature, and duration of heating at the fixed temperature on the formation of spherical leucite crystals obtained by the above procedure are investigated. When the powder mixture of $K_2SO_4 : Al_2(SO_4)_3 : SiO_2 = 5.9 : 1.0 : 1.1$ (mol%) is heated at 1000°C for 3 h, spherical leucite crystals of diameter 70–110 μm (average diameter: 84 μm) form. Upon increasing the duration of heating at 1000°C, the average diameter of the spherical leucite crystals increases, reaching 115 μm after 12 h.

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1. Introduction

Since leucite ($KAlSi_3O_6$) ceramics have excellent aesthetic properties and superior biocompatibility, they have been added to dental porcelain and dental glass materials including tooth crowns as a reinforcement.^{1,2)} In a study of dental glass material, the surface crystallization of leucite was also investigated.³⁾ Further, leucite is expected to be used as a reinforcement for metal materials due to its high melting point (1693°C⁴⁾) and high thermal expansion coefficient (pure leucite: $3.1 \times 10^{-5}/^\circ C$).^{2),5)–7)} However, a method for synthesizing leucite particles that grow in a fixed direction such as whiskers and platelets has not yet been reported.

In an attempt to fabricate leucite particles of arbitrary shape, in the present study, a method for synthesizing novel spherical leucite crystals was investigated. The spherical leucite crystals can improve the mechanical properties when they are added to dental or metal materials. Generally, it is known that spherical filler disperses easily inside a matrix phase. However, there are few reports on the synthesis of a ceramic spherical filler. It is expected that the study of composites reinforced by spherical leucite particles will enable clarification of the effect of ceramic spherical filler on the mechanical properties of composites.⁸⁾

In order to synthesize spherical leucite crystals, powder mixtures consisting of K_2SO_4 , $Al_2(SO_4)_3$ and SiO_2 were used. The effects of the mixing ratios of the raw materials, heating temperature, and duration of heating at the fixed temperature on the formation of the spherical leucite crystals were investigated. Furthermore, the growth process of the spherical leucite crystals was discussed.

2. Experimental procedure

As raw materials, aluminum sulfate hydrate ($Al_2(SO_4)_3 \cdot 14-18H_2O$), silica (flakelike amorphous, mean particle size: 10 μm), and potassium sulfate (K_2SO_4) of reagent grade were used. The $Al_2(SO_4)_3 \cdot 14-18H_2O$ was heated in air to form $Al_2(SO_4)_3$. After heating at 300°C for 12 h, $Al_2(SO_4)_3 \cdot 14-18H_2O$ changed to $Al_2(SO_4)_3$. Starting powder mixtures were prepared by mixing the raw materials at various ratios in acetone and drying them. Each of the starting powder mixtures (approximately 20 g) was placed in an alumina crucible (height: 70 mm, diameter: 50 mm) and covered

with an alumina lid. The crucible was heated in an electric furnace at the rate of 10°C/min until a preselected temperature was reached at which it was maintained for various periods. After heating, the crucible was cooled in the furnace to room temperature. A reactant mass, remaining at the bottom of the crucible, was soaked in 1 mol HCl at 70–80°C for 0.5–1 h. Subsequently, by washing with water and drying the residue, white particles were obtained. The crystalline phase of the particles was examined by X-ray diffraction (XRD) and the morphology was observed by a scanning electron microscope (SEM). The XRD examination was performed under the same conditions for all the experiments. In the case of each of the experimental conditions, the average size of 25 leucite particles was used. In order to elucidate the growth process of the spherical leucite particles, differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out for the mixture of $K_2SO_4 : Al_2(SO_4)_3 : SiO_2 = 5.9 : 1.0 : 1.1$ (mol%) heated up to 1000°C at the rate of 10°C/min and maintained for 3 h at 1000°C in air.

3. Results

3.1 Formation of leucite spheres

Figure 1 shows the compositional ratios of the raw materials that formed solely leucite crystal after heating at 1000°C for 3 h. In Fig. 1, large dots denote the compositions that yielded solely the leucite crystal. In contrast, small dots denote the compositions that yielded not only leucite, but also mullite. Furthermore, in the case of the composition containing the highest ratio of silica, small peaks of mullite and a halo peak that appears to correspond to the amorphous silica of a raw material were observed. Leucite crystal was not formed in this case. As a sample composition yielding solely leucite crystal, the powder mixture of $K_2SO_4 : Al_2(SO_4)_3 : SiO_2 = 5.9 : 1.0 : 1.1$ was selected. Figure 2 shows SEM microimages of the leucite particles that formed by heating the powder mixture at 1000°C for 3 h (a, b) and the fractured surface of the leucite particle (c). Most of the particles were spheres of a diameter 70–110 μm and of average diameter 84 μm . It was observed that sometimes several spheres cohered with each other to form a single particle. Although the surfaces of the spheres appeared to be smooth, detailed observation revealed steps

Fig. 1. Compositional ratios of the raw materials that formed leucite crystal after they were heated at 1000°C for 3 h and then treated with hot HCl.

at the surfaces as seen in Fig. 2(b). In the present paper, these particles are referred to as spherical leucite crystals. As seen in Fig. 2(c), the spherical leucite crystal structure was dense. The leucite particles that were formed using other compositions yielding solely the leucite crystal, as shown in Fig. 1, also exhibited the spherical shape. Thus, the $\text{K}_2\text{SO}_4 : \text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 = 5.9 : 1.0 : 1.1$ was selected as the starting powder mixture composition.

3.2 Effect of heating temperature

Figure 3 shows the XRD patterns of the samples obtained by heating the starting powder mixture at 900, 1000 and 1100°C for 3 h. Figure 4 shows SEM microimages of the samples obtained by heating the starting powder mixture at 900 and 1100°C for 3 h. For comparison, Fig. 2 shows SEM microimages for heating at 1000°C. At the heating temperature of 900°C, solely the leucite crystalline phase was observed, but the peak intensities were relatively weak. In the SEM microimage of 900°C in Fig. 4, fine particles and aggregations were observed, but spherical particles were not. At 1100°C, the crystalline phase was not only leucite, but also mullite. In this case, aggregations composed of fine particles and dense large particles, not of spherical shape, were observed. Consequently, it can be concluded that heating temperature has an important effect of forming leucite spheres, and the optimal heating temperature was determined to be 1000°C.

3.3 Effect of duration of heating

The formation time of the spherical leucite crystals was investigated. Figures 5 and 6 show SEM microimages and XRD patterns of the samples obtained by heating the starting powder mixture at 1000°C for 0, 1, 2 and 12 h, respectively. In the sample obtained by heating up to 1000°C and then cooling rapidly to room temperature, fine particles and aggregations were observed, but spherical particles were not found. According to the XRD pattern of the sample of 0 h heating at 1000°C in Fig. 6, solely a halo diffraction peak that appears to correspond to the amorphous form was observed, but diffraction peaks indicating a leucite crystal were not detected. Spherical particles were observed for the sample obtained by heating at 1000°C for 1 h. However, the number of spherical particles was small and the intensities of diffraction peaks indicating leucite crystal were weak. The halo diffraction peak indicating an amorphous form was also observed. As for the sample heated for 2 h, a large number of spherical particles was formed in the sam-

Fig. 2. SEM microimages of leucite particles formed by heating the starting powder mixture of $\text{K}_2\text{SO}_4 : \text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 = 5.9 : 1.0 : 1.1$ at 1000°C for 3 h (a, b) and the fractured surface of the leucite particle (c).

Fig. 3. XRD patterns of the samples obtained by heating the starting powder mixture at 900, 1000 and 1100°C for 3 h which were then treated with hot HCl.

ple, the crystalline phase of the sample was identified as solely leucite and the diffraction peaks indicating leucite

Fig. 4. SEM microimages of the samples obtained by heating the starting powder mixture at 900 and 1100°C for 3 h which were then treated with hot HCl.

crystal became stronger. In contrast, a halo diffraction peak was not observed. As a result, it is clarified that heat treatment at 1000°C for more than 2 h is required in order to obtain a large number of spherical leucite particles.

Moreover, the effect of heating for more than 2 h at 1000°C on the morphology and the size of the leucite particles was investigated. According to the XRD pattern of the sample obtained by heating at 1000°C for 12 h in Fig. 6, the crystalline phase was solely leucite. The morphology of the leucite crystals was similar to that of the spherical leucite crystals formed by heating at 1000°C for 2 h, as shown in Fig. 5(c). However, a difference between their sizes was identified. Figure 7 shows the average diameter of the spherical leucite crystals formed by heating at 1000°C for 2–12 h. The average diameter increased as the duration of heating was extended, reaching 115 μm after 12 h.

Fig. 6. XRD patterns of the samples obtained by heating the starting powder mixture at 1000°C for 0, 1, 2 and 12 h which were then treated with hot HCl.

Fig. 5. SEM microimages of the samples obtained by heating the starting powder mixture at 1000°C for (a) 0, (b) 1, (c) 2 and (d) 12 h which were then treated with hot HCl.

Fig. 7. Change in average diameter of spherical leucite crystals obtained by heating the starting powder mixture at 1000°C with duration of heating.

3.4 Phase change during heating

Figure 8 shows the DTA curve up to 1000°C and the XRD patterns of the samples heated to 610 and 650°C and quenched to room temperature. In the DTA curve, two endothermic peaks (590 and 640°C) were observed. For the sample heated to 610°C, the main crystalline phases were the same as in the starting powder mixture, namely $\text{Al}_2(\text{SO}_4)_3$ and K_2SO_4 . On the other hand, for the sample heated to 650°C, the crystalline phases were identified as K_2SO_4 and $\text{K}_3\text{Al}(\text{SO}_4)_3$. The sample became spherical and its surface appeared lustrous during shrinking.

Figure 9 shows the TG curves of K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$ and the starting powder mixture that were heated to 1000°C and then maintained at that temperature for 3 h and the XRD pattern of the starting powder mixture that was heated at 1000°C for 3 h. The weight loss of K_2SO_4 was slight, whereas rapid thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ began above 800°C. In

Fig. 9. TG curves of K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, and the starting powder mixture that were heated to 1000°C and then maintained for 3 h and the XRD pattern of the starting powder mixture that was heated at 1000°C for 3 h.

contrast, rapid weight loss of the starting powder mixture occurred above 900°C and almost ceased at 1000°C for 1 h, reaching approximately 17.0 mass%. The XRD examination revealed that the main crystalline phases of the sample were leucite and K_2SO_4 .

4. Discussion

4.1 Formation of leucite crystals

The causes of the two endothermic peaks (590 and 640°C) seen in Fig. 8 are discussed. Because the crystalline phases at 610°C were almost the same as those of the starting powder mixture before heating, the endothermic peak of 590°C is considered to be caused by the transformation of K_2SO_4 from the β -phase (low temperature form) to the α -phase (high temperature form).^{9),10)}

Up to date, the phase diagram for the $\text{Al}_2(\text{SO}_4)_3$ - K_2SO_4 system has not been studied. Therefore the cause of the endothermic peak at 640°C is not clear. However, since the sample that was heated to 650°C shrank, became spherical and had a lustrous surface, the endothermic peak at 640°C is considered to be caused by the formation of a liquid phase. The melting point of $\text{K}_3\text{Al}(\text{SO}_4)_3$ that was detected in the sample after heating at 650°C, as shown in Fig. 8, is reported as 690°C.¹¹⁾ The $\text{K}_3\text{Al}(\text{SO}_4)_3$ is considered to be crystallized from the liquid phase during cooling. There is a possibility that the eutectic point between K_2SO_4 ^{9),10)} and $\text{Al}_2(\text{SO}_4)_3$ is approximately 640°C.

The mass loss of 17.0% after heating the starting powder mixture at 1000°C for 1 h mainly corresponds to the calculated mass ratio of $\text{SO}_3(\text{g})$ from the $\text{Al}_2(\text{SO}_4)_3$ in the starting powder mixture (16.7%). Therefore the mass loss is considered to be caused by the decomposition of $\text{Al}_2(\text{SO}_4)_3$ as given by the following equation.

Before HCl treatment, leucite and K_2SO_4 were identified in the sample heated at 1000°C for 3 h. After HCl treatment, other than spherical particles, fine particles were also observed, as seen in Figs. 5(a) and (b). The particles are

Fig. 8. DTA curve of the starting powder mixture heated up to 1000°C at the rate of 10°C/min and the XRD patterns of the powder mixture that was heated to 610 and 650°C and then rapidly cooled to room temperature.

considered to be formed by the reaction between the Al_2O_3 , generated according to Eq. (1), and the amorphous SiO_2 of the raw material. Furthermore, the Al_2O_3 - SiO_2 particles are believed to be uniformly scattering in the liquid phase whose main component is K_2SO_4 .

4.2 Growth process of spherical leucite crystals

After the starting powder mixture was heated at 1000°C for 12 h, spherical particles were mainly observed, as shown in Fig. 5, and solely leucite crystal was identified, as shown in Fig. 6. In contrast, the fine particles decreased with an increase in the duration of heating. As a result, the spherical particles are determined to be leucite crystal and are considered to be formed from the fine particles. As the nucleation of leucite begins, the crystal shape is considered to be spherical, because the crystal is surrounded by the K_2SO_4 liquid, which results in the disadvantage of high surface energy. The growth process of the spherical leucite crystal is shown in Fig. 10. In the beginning, the fine particles surrounding the leucite crystal react with the K_2SO_4 liquid to precipitate leucite crystal at the surface of the

original crystal. Consequently, for a short time, the particles around the original crystal decrease in quantity, so that near the surface, the growing leucite crystal is filled with the liquid phase. Therefore, the leucite particle is thought to maintain a spherical shape. However, the leucite crystal is again immediately surrounded by the particles. This process is thought to occur repeatedly, thus resulting in continuous growth of the spherical leucite crystals. The growth of the spherical leucite crystals with the increase in the duration of heating, as seen in Fig. 7, is considered to be caused by the cohesion of several spherical leucite crystals, as seen between the crystals of A and B in Fig. 5(d), except for the further crystallization of leucite as in the above-mentioned process.

5. Conclusions

When a powder mixture consisting of $\text{Al}_2(\text{SO}_4)_3$, SiO_2 and K_2SO_4 was heated at 1000°C , dense spherical leucite crystals were formed. In the case of heating the powder mixture of $\text{K}_2\text{SO}_4 : \text{Al}_2(\text{SO}_4)_3 : \text{SiO}_2 = 5.9 : 1.0 : 1.1$ (mol%) at 1000°C for 3 h, spherical leucite crystals of 70 – $110\ \mu\text{m}$ diameter and $84\ \mu\text{m}$ in average diameter were obtained. With increasing the duration of heating at 1000°C , the average diameter of the spherical leucite crystals increased, reaching $115\ \mu\text{m}$ after 12 h.

Fig. 10. Schematic diagram of the growth process of the spherical leucite crystals.

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