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Preparation of $CaSiO_3$ whiskers from alkali halide fluxes

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Abstract

$CaSiO_3$ whiskers were prepared from fine $CaSiO_3$ powder by use of alkali halide fluxes, NaCl, KCl, and their mixture. The $CaSiO_3$ powder and the flux were mixed and heated at temperatures from 850 to 1000°C for 1 to 48 h. The average lengths, diameters and aspect ratios ranged from 3.24 to 10.5 μm, 0.33 to 1.12 μm and 7.1 to 21.7, respectively. The diameter of the whiskers increased with increasing heating temperature more rapidly than the length, so that the aspect ratio decreased with increasing temperature. The whiskers were considered to grow by an Ostwald ripening mechanism. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Aspect ratio; $CaSiO_3$; Flux growth; Whiskers

1. Introduction

$CaSiO_3$ (wollastonite) has been traditionally used as a raw material for tiles or for white paint, as a filler for resins or paper and as an alternative to asbestos. It has also been studied as an additive to porcelain,[1] as high-frequency insulators[2] and as machinable ceramics.[3] $CaSiO_3$ belongs to the pseudopyroxene group and three polymorphs, i.e. wollastonite, pseudowollastonite and parawollastonite, have been identified. The shape of $CaSiO_3$ particles tends to be acicular or platey reflecting the crystallographic structure, and some applications make use of this character. For example, $CaSiO_3$ machinable ceramics comprise a sintered body with high porosity formed by the intersection of acicular particles.[3] The size and the aspect ratio of natural wollastonite particles are limited by the condition of the deposits, but if the material can be synthesized artificially and its size and aspect ratio can be controlled, then new applications such as fillers for engineering plastics and for bioactive materials with superior toughness will become possible.

Setoguchi et al. have synthesized single crystals of $CaSiO_3$ by the flux method.[4] Columnar $CaSiO_3$ grains with length 6 mm and diameter 0.3 mm were synthesized by the use of an alkali halide. Fine $CaSiO_3$ whiskers are expected from the same method under different conditions, for example, from different types of raw materials and firing conditions.

In this study, fine $CaSiO_3$ whiskers were prepared by the flux method using fine $CaSiO_3$ powder, prepared by the coprecipitation method, and alkali halide fluxes, comprising NaCl, KCl and their mixture. The effect of the synthesizing conditions on the size and aspect ratio of $CaSiO_3$ whiskers was investigated.

2. Experimental procedures

2.1. Preparation of starting powder

$CaSiO_3$ starting powder was prepared by the coprecipitation method.[5] The chemicals used were Ca nitrate tetrahydrate and tetraethyl orthosilicate (TEOS). They were dissolved in ethanol (0.4 mol/dm^3) and used as a starting solution. Precipitate was obtained by the addition of 25% NH_4OH solution in the same amount as

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the starting solution. The precipitate was dried with a hot water bath and later in an oven at 100°C, and then calcined at 500°C for 2 h. The calcined precipitate was ground with a mortar and a pestle.

2.2. Growth of $CaSiO_3$ whiskers in alkali halide fluxes

The starting powder (0.2 g) was mixed with an alkali halide flux (8 g) with an agate mortar and a pestle. Sodium chloride, potassium chloride, and a 1:1 mixture of these were used as fluxes. These series will be referred as the NaCl, KCl and NaCl + KCl series, respectively. The mixed sample was heated in a porcelain crucible with an electric furnace. The crucible was placed in a larger crucible and 5 g of the flux was stuffed between the inner and the outer crucibles to prevent the evaporation of the flux from the inner crucible during heating. The heating rate was 5°C/min. The cooling rate and soaking time were adjusted from 0.5 to 5°C/min (in some experiments, the sample was quenched in air to room temperature) and from 0 to 48 h, respectively. After the heat treatment, the flux was removed by boiling in water.

2.3. Characterization of synthesized $CaSiO_3$ whiskers

Crystalline phases in the samples were measured by powder X-ray diffraction (XRD, Rigaku Geigerflex) using graphite monochromated CuK_α radiation. The samples were observed by scanning electron microscopy (SEM, Hitachi H-2050S), and the length and diameter of the whiskers were measured from the SEM images using an image analysis program 'NIH Image version 1.6' (National Institute of Health, USA). Before the observations, the samples were dispersed in ethanol by ultrasonic treatment. The resulting suspension was dropped on a small piece of a cover glass, dried and coated by Au sputtering and used for SEM observation.

Transmission electron microscopy (TEM, Hitachi H-900) was also used for the observation of the whiskers. The crystallographic direction of the whisker elongation was determined by electron diffraction.

3. Results and discussion

3.1. Size and aspect ratio of $CaSiO_3$ whiskers

In all experiments, only β-$CaSiO_3$ was identified in the samples by XRD.

SEM micrographs of the whiskers synthesized by use of the three kinds of flux are shown in Fig. 1. The heating temperature, soaking time and cooling rate of these samples were 900°C, 24 h and 5°C/min. In all samples, most of the particles were prismatic. The size distribution was very large, and the lengths were from several to several tens of micrometers whereas the diameters were in the range of submicrometers. In some cases, it was possible to observe particles with coagulates, bunches of whiskers and equiaxial particulates in the samples.

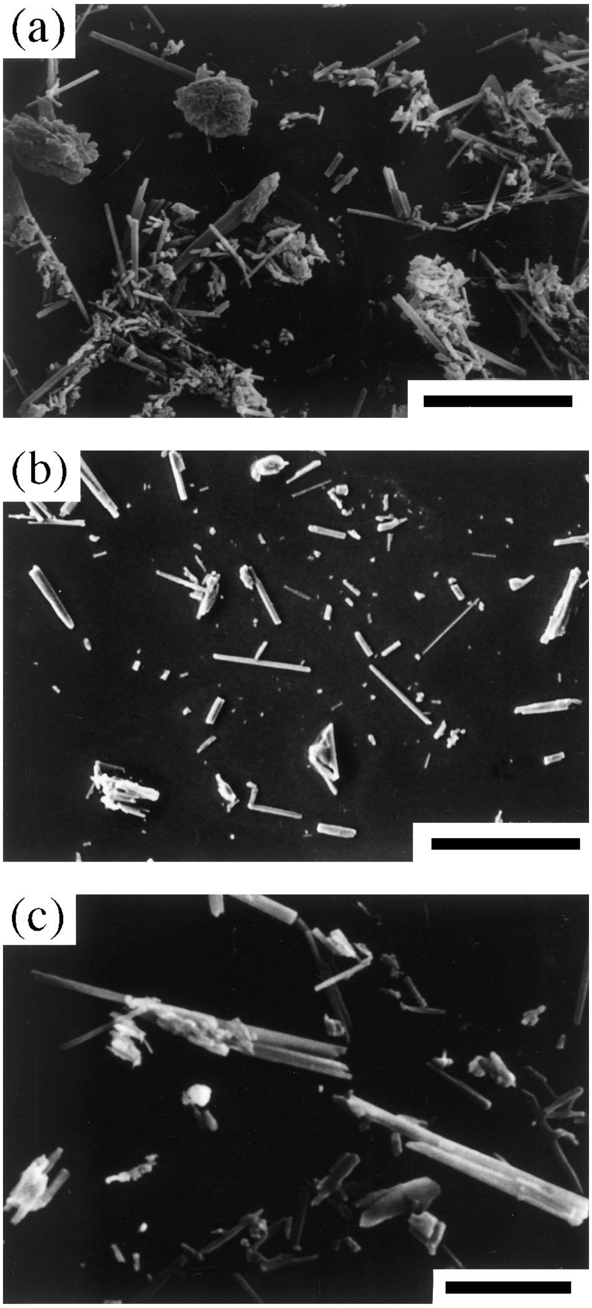

Fig. 1. SEM micrographs of $CaSiO_3$ whiskers prepared from (a) NaCl, (b) KCl and (c) NaCl + KCl fluxes (scale bar = 10 μm). Heating temperature and soaking time were 900°C and 24 h, respectively.

The change of average length, diameter, and aspect ratio of the whiskers as observed by image analysis as a function of heating temperature are shown in Figs. 2–4, respectively. The soaking time was 24 h and the cooling rate was 5°C/min. The error bars in the figures indicate standard deviations. The average lengths and diameters were distributed from 3.2 to 10.5 μm and from 0.33 to 1.12 μm, respectively. The aspect ratios ranged from 7.1

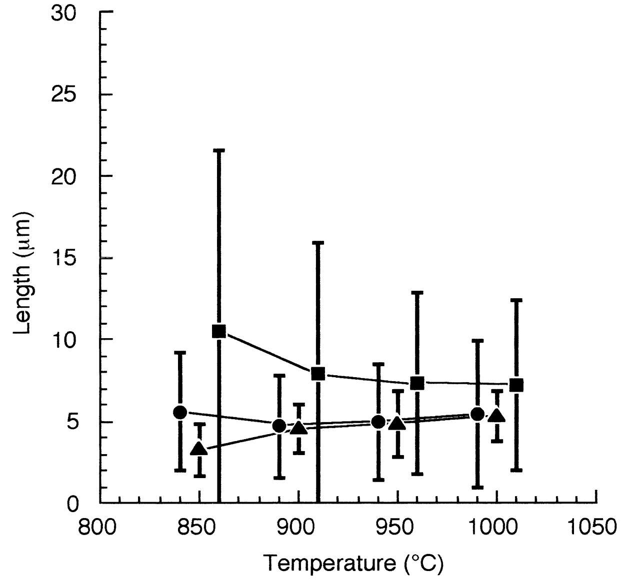

Fig. 2. Changes of lengths of $CaSiO_3$ whiskers as a function of heating temperature prepared from NaCl (●), KCl (▲) and NaCl + KCl (■) fluxes. Soaking time was 24 h.

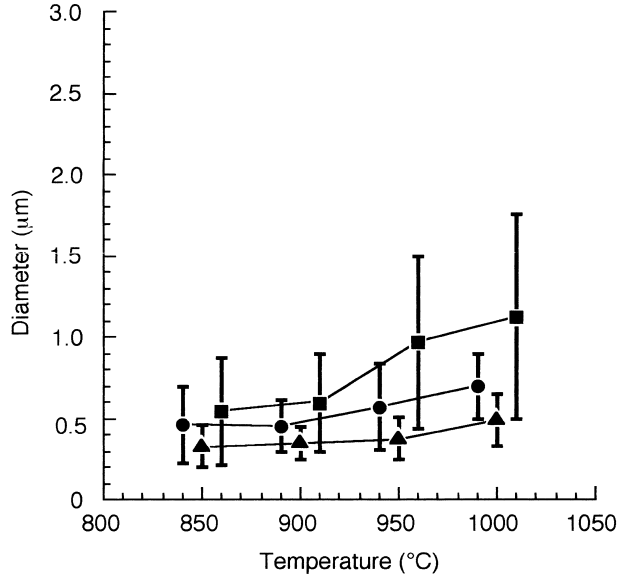

Fig. 3. Changes of diameters of $CaSiO_3$ whiskers as a function of heating temperature prepared from NaCl (●), KCl (▲) and NaCl + KCl (■) fluxes. Soaking time was 24 h.

to 21.7. Since the scattering of the data is very large, it is difficult to discuss in detail the relation between the whisker size and the firing condition of these samples. The following briefly considers the dependence of the average data on the firing temperatures.

The average lengths of whiskers obtained from the NaCl and KCl series were almost similar. On the other hand, the length of whiskers from the NaCl + KCl series was longer than those of NaCl and KCl samples. The length of whiskers is expected to be affected by the mobility of components in the flux, which may be related to the diffusion rate of components and/or the viscosity of the flux during heating. The mobility of components in the NaCl + KCl flux may be larger because the temperature difference between the soaking temperature and the melting point of the flux is much larger in the NaCl + KCl flux than in the others; the melting points of NaCl, KCl and NaCl + KCl (1:1) fluxes are 805, 774 and 645°C. On the other hand, there is not a common trend in the relation between the average length and the heating temperature for each series of sample. In general, however, a heating temperature of 850°C is found to be sufficient for the elongation of $CaSiO_3$ whiskers in this experiment.

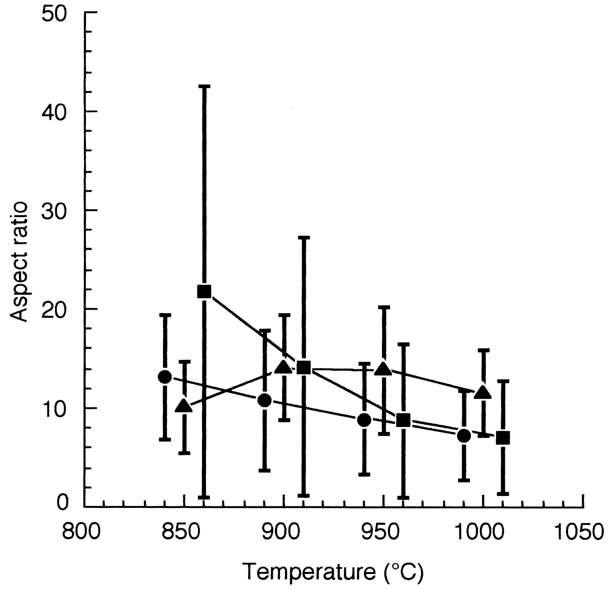

Fig. 4. Changes of aspect ratios of $CaSiO_3$ whiskers as a function of heating temperature prepared from NaCl (●), KCl (▲) and NaCl + KCl (■) fluxes. Soaking time was 24 h.

The average diameters of NaCl + KCl samples were also larger than those of NaCl and KCl series (Fig. 3). This can be explained similarly as for the variation of the length. In contrast to the case of the length, the average diameters of the NaCl series were larger than those of the KCl series. In addition, the average diameters clearly increased with increasing heating temperature. With respect to diameter, the effects of the kind of flux and heating temperatures are more clearly observed than with the length data. In the data of length, the fracture of whiskers during handling and/or the spacial hindrance in the growth may prevent the clear tendency.

Reflecting the data of the length and the diameter, the average aspect ratio decreased with heating temperature in almost all cases except in the data for the KCl flux from 850 to 900°C (Fig. 4). From these results, a relatively low temperature is preferable to prepare whiskers with high aspect ratio.

3.2. Mechanism of whisker growth

The effect of soaking time, and cooling rate on the length and diameter of the whiskers prepared by use of NaCl flux are illustrated in Figs. 5 and 6, respectively. Here, the heating temperature was 1000°C, the cooling rate was 5°C/min (Fig. 5) and the soaking time was 12 h (Fig. 6). The average length and diameter increased with increasing soaking time, but did not show a clear dependence on the cooling rate. For the KCl and NaCl + KCl fluxes, a similar trend was observed. These results indicate the special character of the whisker formation in this study. That is, in the usual 'flux method', the starting material completely dissolves into the flux during the soaking time and the product crystals are obtained during the cooling process. In this experiment, however, the solubility of $CaSiO_3$ in the alkali halide fluxes may be very low; the solubility of $CaSiO_3$ in NaCl melt has been reported to be as low as 0.09 mass% at 1010°C[4] though there are no reported data for KCl and NaCl + KCl mixtures. Therefore, the starting material is considered not to dissolve completely into the flux. This suggests that the whiskers may mainly grow by an Ostwald ripening mechanism, i.e., the dissolving of fine particles and the depositing of components on larger particles. This is the reason why the whiskers grew not during the cooling process but grew during the soaking of the melt.

When Ostwald ripening is the dominant mechanism of the whisker growth, the character of the starting material, for example, the particle size and/or chemical activity, must affect the growth of whiskers because the dissolution rate of the material depends upon such characters. We checked this point by use of a different type of $CaSiO_3$ starting material. Fig. 7. illustrates a SEM micrograph of the product prepared from $CaCO_3$ and amorphous SiO_2 powders; these had the particle sizes of several tens of micrometers using NaCl flux. The heating temperature was 1000°C, the soaking time was 12 h and the cooling rate was 5°C/min. The obtained material consisted of β-$CaSiO_3$ particles with average diameter of several tens of micrometers, some particles being columnar rather than whisker-like. From another type of $CaSiO_3$ powder (α-$CaSiO_3$) synthesized by conventional solid-reaction method with the diameter of several tens of micrometers, a similar result was obtained. These results support the above discussion, i.e., $CaSiO_3$ whiskers can be obtained only from fine starting powders. Since the specific surface area of the coprecipitated powder measured by BET method was 27 m^2/g and the primary particle diameter observed by TEM was around 0.1 μm, the starting powder was considered to

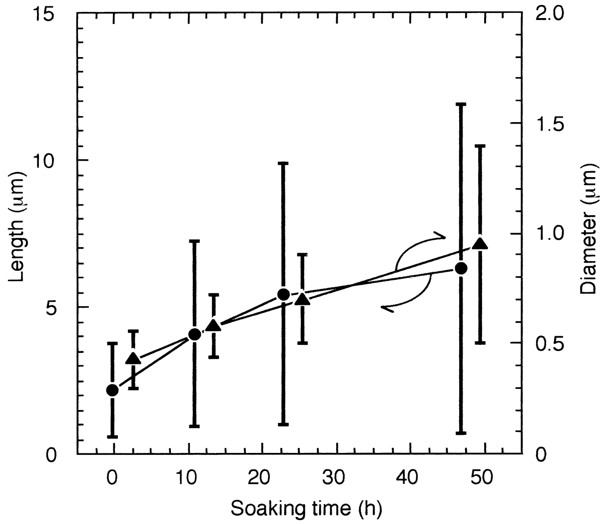

Fig. 5. Effect of soaking time on the length (●) and the diameter (▲) of $CaSiO_3$ whiskers prepared from NaCl flux. Heating temperature was 1000°C.

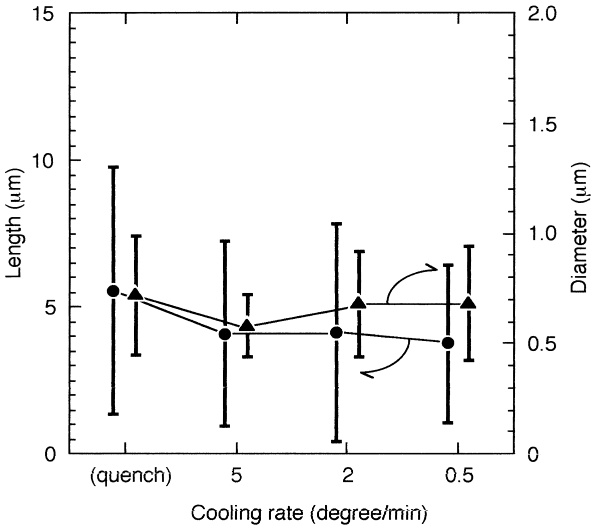

Fig. 6. Effect of cooling rate on the length (●) and the diameter (▲) of $CaSiO_3$ whiskers prepared from NaCl flux. Heating temperature and soaking time were 1000°C and 12 h, respectively.

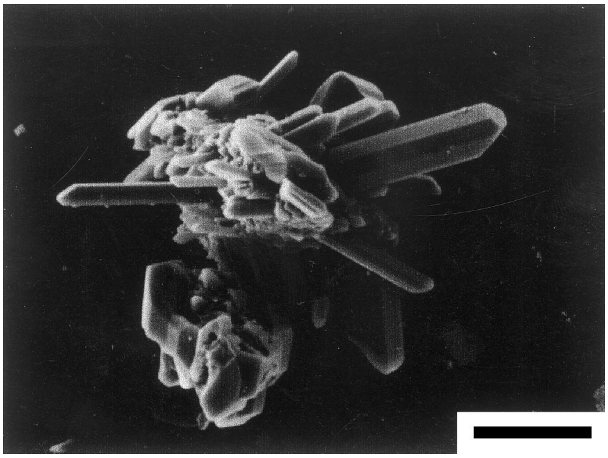

Fig. 7. SEM micrograph of $CaSiO_3$ sample prepared from NaCl flux using $CaCO_3$ and amorphous SiO_2 powders (scale bar = 10 μm).

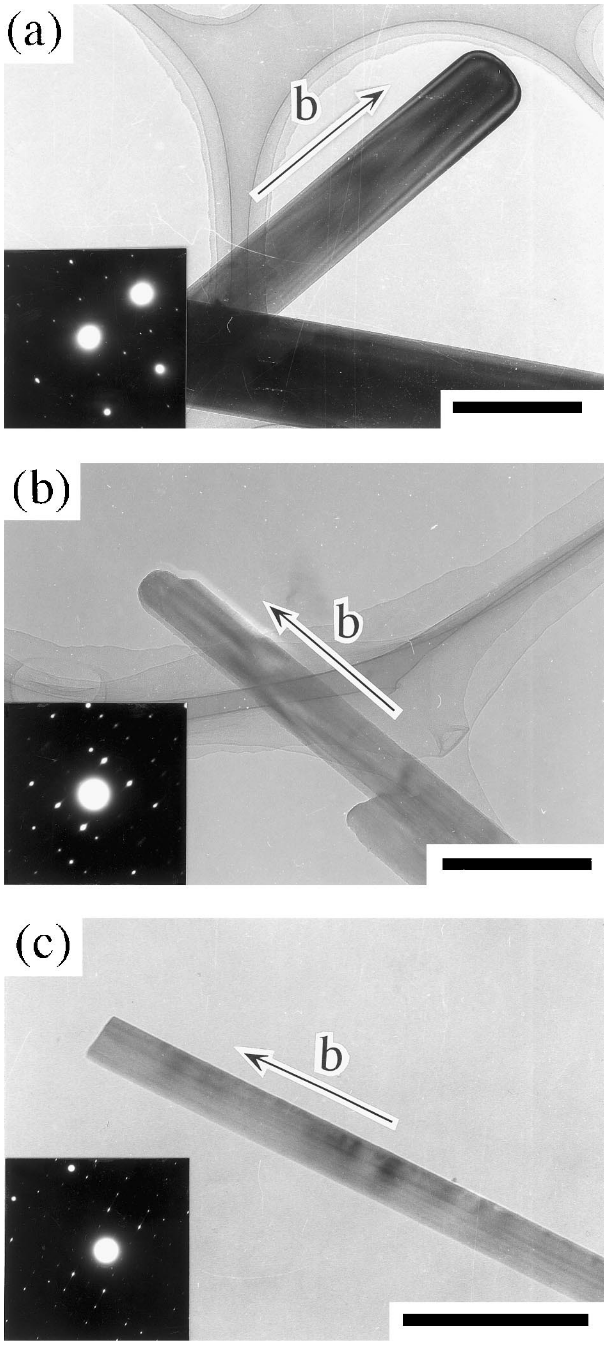

Fig. 8. TEM micrographs and electron diffraction patterns of $CaSiO_3$ whiskers prepared from (a) NaCl, (b) KCl and (c) NaCl + KCl fluxes (scale bar = 0.5 μm).

be fine and active, thus, $CaSiO_3$ whiskers were prepared successfully only from this powder.

TEM photographs and electron diffraction patterns of the whiskers are shown in Fig. 8. The diffraction patterns show that the whiskers were single crystals. Both wollastonite 2M [monoclinic type, Fig 8(a) and (c)] and 1Tr [triclinic type, Fig. 8(b)] crystal phases (they are classified in β-$CaSiO_3$) were found in the three series of samples. The elongated direction was along the *b*-axis in both types, which corresponds to the direction of the single chain of SiO_4 tetrahedra. This result agrees with the case for $CaSiO_3$ single crystal prepared by flux growth[4] and by the thermal decomposition of xonotlite[6].

4. Conclusion

$CaSiO_3$ whiskers were prepared by use of alkali halide fluxes, i.e. NaCl, KCl and their mixture, starting from $CaSiO_3$ fine powder prepared by the coprecipitation method. Their average length, diameter, and aspect ratio ranged from 3.24 to 10.45 μm, 0.33 to 1.12 μm, and 7.1 to 21.7, respectively. Since there was a tendency to increase the diameter more than the length with increasing heating temperature, the aspect ratio decreased with increasing heating temperature. The whiskers were considered to grow by an Ostwald ripening mechanism during heating treatment. The direction of whisker growth was parallel to the *b*-axis corresponding to the chain of SiO_4 tetrahedra.

Acknowledgements

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