Influence of Melting Temperature on Morphology of Primary Mullite in $\text{SiO}_2\text{-Al}_2\text{O}_3$ System

H. Nakae, S. Nakano[†] and M. Yoshida^{††}

Department of Materials Science and Engineering, School of Science and Engineering,
Waseda University, Tokyo 169, Japan

A series of melting and solidification experiments were carried out using high-purity SiO_2 and Al_2O_3 powders as the starting materials. The effect of melting temperature on the morphology of the primary mullite was investigated. The following conclusions were made:

- 1) The morphology of the primary mullite went through five stages as the melting temperature increased; massive, fibrous, faceted dendritic, feathery and fine feathery structures. These phenomena can be explained based on the number of effective nuclei in the melt.
- 2) The fibrous mullite grew from mullite precursors formed in the melt. Under highly supercooled conditions, the fibrous morphology becomes unstable and begins to branch and form a faceted dendritic crystal.
- 3) When the number of nuclei is extremely small, the mullite nucleated on the rhombic dodecahedron Mo originating from the molybdenum crucible and crystallizes out into a feathered structure.

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I. Introduction

The solidification phenomenon of certain ceramic eutectic systems can be handled in the same manner as that of a metal system⁽¹⁾. However, because the diffusivity in the melt of ceramic systems is lower than that of metal systems, growth kinetics of the crystal should be larger than that in metal systems. One of the authors previously reported the formation of fibrous mullite from a hyper-eutectic silica/mullite melt⁽²⁾, and observed the formation of dendritic mullite under certain melting conditions. The morphology of the dendritic mullite, however, was significantly different from that of the metal dendrite⁽³⁾. The morphology of the dendritic mullite was a fibrous-faceted dendrite. Accordingly, a series of experiments was performed to clarify the conditions under which a dendrite of this shape is formed.

II. Experimental Methods

To minimize contamination from impurities, 99.99 mass% SiO_2 powder (amorphous, 74 μm mean particle diameter) and 99.99 mass% $\alpha\text{-Al}_2\text{O}_3$ powder (0.98 μm mean particle diameter) were used as the starting materials in the experiments. Their chemical compositions are shown in Table 1. These two types of powders were mixed to given compositions (11 to 24 mass% Al_2O_3), and blended for 48 h in a dry ball mill. In a previous experiment⁽²⁾, a wet ball mill was used for the blending and the

Table 1 Chemical composition of starting materials (mass ppm).

Impurities	Fe	Mg	Na	Al	Si	Ca	Cr	Ni
$\text{SiO}_2 > 4\text{N}$	10	20	10	10	—	40	—	—
$\text{Al}_2\text{O}_3 > 4\text{N}$	7	1	3	—	18	—	1	1

blended material was cast in a plaster mold. However, to avoid contamination from the plaster, blending was carried out in a dry ball mill using a polystyrene pot and high-purity alumina balls. As in the previous report⁽²⁾, the resultant blended powder was melted and solidified in an 8 mm inner diameter, 12 mm high molybdenum crucible set in a high-purity Al_2O_3 Tammann tube with a graphite susceptor. In this study, the temperature was raised in two stages. Initially, the temperature was raised at a rate of 6.5 K/min up to a temperature 60 K lower than the predetermined melting temperatures. Thereafter, in order to minimize overheating, the blended powder was heated slowly for 14.4 ks to a given melting temperature. After holding the melt at the given melting temperature for 7.2 ks, it was cooled to 1673 K at a rate of 1 K/min, followed by further cooling in the furnace. In part of the experiments, the solidified or molten specimens were quenched to observe the growth morphology of mullite in the course of solidification and the resultant solid materials in the melts. The atmosphere for melting was argon. After the melting and solidification experiment, the solidified specimen within the molybdenum crucible was cut, polished, etched and ion-coated with Au-Pd for SEM observation, EDX-WDX analysis and for micro-X-ray diffraction, MDG ($\text{CuK}\alpha$ collimator diam.=50 μm). Etching was carried out for about 20

[†] Graduate Student, Waseda University. Present address: Suzuki Motors Corp., Hamamatsu 432, Japan.

^{††} Graduate Student, Waseda University.

min in 20 vol% HF aqueous solution to emboss the crystallized mullite. Unless otherwise noted, the structure of the specimen was observed in its central portion.

III. Experimental Results

Figure 1 shows the representative structures of the 15 mass% Al_2O_3 specimens indicating the effect of the melting temperatures. Figure 1 explains the morphologies of the primary mullite melted at 1953, 1969, 1979, 1998, 2036 and 2063 K.

- a) at 1953 K: co-existence of massive and fibrous structures
- b) at 1969 K: fibrous structure
- c) at 1979 K: co-existence of fibrous and faceted dendritic structures
- d) at 1998 K: faceted dendritic structure
- e) at 2036 K: feathered structure
- f) at 2063 K: fine feathered structure.

From these results, it was revealed that crystallized mullite changes stepwise with the rise in the melting temperature as follows:

massive $\rightarrow$ fibrous $\rightarrow$ faceted dendritic $\rightarrow$ feathered
 $\rightarrow$ fine feathered (or amorphous: 11 mass% Al_2O_3 , 2000 K).

According to macroscopic observations of the cross sections of these specimens, the specimens from a) to e) were cloudy, but specimen f) was almost transparent and glassy except for its central portion.

Fibrous mullite has been previously⁽³⁾ described, but the authors' previous report⁽²⁾ is probably the first one to describe faceted dendritic mullite. The high-magnification SEM images for a), c) and f) of Fig. 1 are shown in Fig. 2. The coexistence of the massive and fibrous structures in Fig. 1 a) can be clearly understood by referring to the high-magnification photograph given in Fig. 2 a). The enlarged structure of the fibrous portion of the fibrous-faceted dendritic structures in Fig. 2 c) shows the start of branching at the edge of a fiber. In Fig. 2 f), the structure observed in the matrix appears to be composed of very fine feathered crystals.

The results of these experiments were arranged from the viewpoint of the relation between the melting temperatures and the alumina concentrations for crystallized mullite morphology which is shown in Fig. 3. The figure indicates that the changes in the growth morphologies of the primary mullite described in Fig. 1 does not depend on the alumina concentration, but on a characteristic tendency in a $\text{SiO}_2/\text{Al}_2\text{O}_3$ system. In the previous report⁽²⁾, faceted dendrites were formed only in the 14.7 mass%

Fig. 1 Influence of melting temperature on mullite morphology (15 mass% Al_2O_3 , holding time 7.2 ks).

Fig. 2 SEM images of mullite morphology magnifying Figs. 1(a), (c) and (f).

Fig. 3 Influence of melting temperature and alumina concentration on mullite growth morphology.

Al_2O_3 mixture possibly because of an inadequate temperature range selection.

IV. Discussion

1. Crystallized material at melting temperature

As described in a preceding section, the coexistence of the fibrous and dendritic microstructures was found under the following melting conditions (15 mass% Al_2O_3 at liquidus temperature of 1998 K). To examine the existing materials at the melting temperature, that may be heterogeneous nucleation sites of the primary mullite, the same material was melted at 1998 K and quenched from the same temperature. The specimen was then subjected to surface analysis using an SEM and an EPMA. The results are given in Fig. 4, which shows many crystallized materials with a diameter of about $1\text{ }\mu\text{m}$ in the glass matrix. Figures 4(c) and (d) are the results of the area

compositional analyses of (b). Although the materials in Fig. 4(b) were conjectured to be the primary mullite, the difference in the composition between the materials and the glass matrix could not be distinguished by EPMA. Mullite could also not be identified using the X-ray diffraction pattern of the powdered specimen. Therefore, the materials are still an unknown matter.

In the other crystallized material, two fine Mo crystals were found under the observed surface in Fig. 4. The crystals were accidentally found in the specimen, and the existence of the Mo crystals was confirmed within almost all the specimens by careful SEM observation. A typical example is shown in Fig. 5 that shows the results of the linear compositional analysis. The shape of the Mo crystals is rhombic dodecahedron. With EPMA, oxygen and carbon were analyzed using WDX as well as EDX; however, no element except Mo was detected. Further, microbeam X-ray diffraction (MDG) revealed that these crystallized materials are Mo bcc crystals (see Fig. 6).

2. Growth of fibrous mullite during cooling

As shown in Fig. 1, in 15 mass% Al_2O_3 , melted and held at 1979 K, the fibrous and faceted dendritic mullite simultaneously existed. To observe the growing process of the primary mullite, specimens that were melted and held under the same melting conditions as previously mentioned were quenched during cooling. The results shown in Fig. 7 suggest that many fine crystal-like materials are dispersed at 1973 K and that fibrous mullite crystallizes at 1873 K, and begins to branch at 1823 K. The matrix of the specimen quenched at 1823 K was still glassy, although the temperature is lower than the silica/mullite eutectic temperature. Therefore, faceted dendritic mullite is thought to be formed as a result of the branching of the primary mullite under the highly supercooled conditions. Observations of the structure at 1873 K suggest the existence of a petal-like fine crystal (shown by the arrow), and an enlarged photograph of this is given in Fig. 8. Although the sizes are different, the same crystals were found in all specimens in Fig. 7 and partly in Fig. 4. A further study of Fig. 4 indicates that the

Fig. 4 SEM images and EPMA analyses of 15 mass% Al_2O_3 specimen melted and water quenched at 1993 K; (a) SEM image, (b) magnified image of (a), (c) and (d) area compositional analyses of (b).

Fig. 5 SEM image and EPMA linear analysis of Mo crystal in matrix.

fibrous crystals begin to grow from part of the petal-like crystals. These are considered to be nuclei of the primary mullite (precursors of fibrous mullite). The same materials can be found in Fig. 6 in the preceding paper⁽²⁾.

Risbud and Pask⁽⁴⁾ over heated melts 200 K higher than the liquidus temperature to homogenize them, and the resulting specimens were subjected to crystallization experiments. They reported the existence of massive and fibrous mullites. Their experimental conditions, however, were quite different from ours. Davis and Pask⁽⁵⁾ performed a series of mullite formation experiments us-

Fig. 6 Microbeam X-ray diffraction pattern taken from Mo crystal in matrix (Cu-K α , collimator diam. = 50 μm).

ing the SiO_2 /single crystal Al_2O_3 diffusion couple to observe the formation of mullite at 1910 K or higher. In our experiment, however, the formation of mullite could not be confirmed in the specimen quenched after melting and holding. This difference may arise from the fact that the starting materials used in our experiment were powdery and thereby the melt was more homogeneous than theirs.

3. Growth of faceted dendrite

The state of branching of fibrous crystals is shown in Fig. 2. The 15 mass% Al_2O_3 specimen with the same chemical composition as the specimen used in Fig. 2 was melted at 2003 K, which is between the faceted-dendrite-forming temperature (1998 K) and the feathered-crystal-forming temperature (2036 K), and was then solidified. The resultant structures are shown in Fig. 9. These structures are well arranged in the same direction, suggesting

Fig. 7 Growing process of mullite crystals melted 1997 K and quenched from various temperatures (15 mass% Al_2O_3).

Fig. 8 Magnified petal-like material observed in Fig. 7 arrowed section.

Fig. 9 Faceted dendrite structure of mullite (15 mass% Al_2O_3 , melted 2003 K).

that one faceted dendrite grew from one branched fiber as shown in Fig. 2 c). When discussing the faceted-dendrite-formation in detail as previously mentioned, the degree of branching or the perturbation of the growth interface increased with increasing melting temperature. In general, the branching of the growth interface is caused by supercooling (by the constitutional undercooling), or by supersaturation of the liquid. Accordingly, it seems reasonable to postulate that supersaturation will be induced by increasing melting temperature. One of the ways to accomplish this is to diminishing the equilibrium amount of the primary mullite in the liquid with increasing in melting temperature. Another factor for promoting the perturbation is decreasing the diffusivity of alumina at the growth interface by increasing silica composition discharged from the interface into the liquid, which often results in increasing viscosity of the mixed-oxide liquid⁽²⁾.

The fiber/dendrite transition can be explained by both Kossel-Stranski's two-dimensional nucleation model⁽⁶⁾

Fig. 10 Schematic of relationship between supersaturation σ and growth morphology.

and Burton-Cabrera-Frank's (BCF's) spiral growth mode⁽⁷⁾. The growth rate, R , of a crystal grain is said to be a function of the degree of supersaturation, σ , of a

Fig. 11 Relationship between growth morphology and supersaturation.

melt as shown by Fig. 10⁽⁸⁾⁽⁹⁾. If the degree of supersaturation is equal to the critical value, σ^* or less, the grain grows according to the screw dislocation mechanism (BCF model); whereas, if it exceeds the critical value, the growth rate is controlled by two-dimensional nucleation (K.S. model). Taking into account the Berg effect, it is said that an increase in supersaturation leads to the formation of dendrite (see Fig. 11). Figures 2 and 9 show the dendrite of this morphology, which was transitioned into a faceted dendrite. These trends are in good agreement with the results shown in Fig. 3; namely, the fibrous crystals changed into the faceted dendritic crystals as the melting temperature rose, while further increases in the melting temperature led to the feathered crystals.

4. Feathered crystals

By further increasing in the melting temperature above the liquidus results in the disappearance of the effective nuclei (e.g. the precursors of mullite or the equilibrium amount of primary mullite at melting temperature). As a consequence, the dendrite arm spacing will still decrease

Fig. 12 Feathered mullite crystals nucleated on rhombic dodecahedron Mo crystal in the melt.

by increasing the supercooling of the melt. The morphology of the crystal, feathered crystal is given in Fig. 12, in which the nucleus at the center of the crystals is Mo as shown in Figs. 4 and 5. As the SEM photograph indicates, the mullite nucleates at the edge and on the corner of the rhombic dodecahedron Mo, and grows into the feathered crystal. The Mo, which was dissolved by and crystallized out into the melt probably came from the crucible. In this connection, Mo reportedly forms a eutectic system with oxides⁽¹⁰⁾⁽¹¹⁾, and this seems to signify the dissolution of Mo into the oxide melt followed by crystallization during temperature descent. As can be understood from Fig. 3, the feathered crystal is formed when its melting temperature is higher than that of a faceted dendrite. Under the conditions (15 mass% Al_2O_3 , melting at 1973 K and quenching) shown in Fig. 5, this Mo does not act as the source of nucleation, but only exists in the melt. Therefore, under the conditions in which a faceted dendrite can hardly be formed, Mo seems to act as the nucleus due to the excessive supercooling of the melt. For this reason, the grain growth rate becomes inevitably greater, resulting in the formation of the feathered crystal.

5. Changes in solidification morphology

As explained in the preceding section, the crystallization morphology of mullite changed as follows with the change in the melting and holding temperatures:

massive $\rightarrow$ fibrous $\rightarrow$ faceted dendritic $\rightarrow$ feathered
 $\rightarrow$ fine feathered or amorphous.

From these results, the changes will be closely related to the number of nuclei that decrease as the melting and holding temperature increases, and this will bring about supersaturation of the melt during cooling. Since the growth rate of a crystal is proportional to the degree of supersaturation of the melt, the growth morphology seems to have changed; namely, the area of the crystal growth interface might be increased by branching. For example, it is well known in the solidification of flake graphite cast iron that an increase in the degree of supercooling (or solidification rate) discontinuously changes the solidification morphology⁽¹²⁾ from flake graphite to supercooled graphite. The cause of this phenomenon is thought to be that the solute build-up of the diverging phase in front of graphite/liquid interface, or the supersaturation (or the related undercooling) increases with increasing solidification rate⁽¹³⁾. Accordingly, the perturbation and/or branching of the interface proportionally takes place with respect to the growth rate. The morphological transition we observed this time can be explained in the same way as previously mentioned.

V. Summary

A series of melting and solidification experiments were carried out with high-purity SiO_2 and Al_2O_3 powders used as starting materials. The effects of the melting

temperature on the crystallization morphology of the primary mullite were investigated. The conclusions are as follows:

(1) The fibrous mullite grows from mullite precursors formed in the melt.

(2) Under highly supercooled conditions, the solid/liquid interface of the fibrous mullite becomes unstable, begins to branch and forms the faceted dendritic crystal.

(3) When the amount of nuclei is extremely scarce in the melt, mullite nucleates on the rhombic dodecahedron Mo originating from the crucible and crystallized out in the form of a feathered structure.

1) The crystallization morphology of mullite changes stepwise through five stages as the melting temperature rises; massive, fibrous, faceted dendritic, feathery and fine feathered (or amorphous) structure. These phenomena can be explained based on the number of effective nuclei.

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