Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 579–583
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Mullite whiskers derived from kaolin

B.M. Kim [a], Y.K. Cho [a], S.Y. Yoon [a], R. Stevens [b], H.C. Park [a,*]

[a] Department of Materials Science and Engineering, Pusan National University, Pusan 609-735, South Korea
[b] Department of Mechanical Engineering, University of Bath, Bath BA2 97AY, UK

Received 19 September 2007; received in revised form 30 October 2007; accepted 10 January 2008
Available online 24 April 2008

Abstract

Short mullite whiskers prepared by firing compacts of kaolin and $NH_4Al(SO_4)_2{\cdot}12H_2O$ powders, with a small addition (0.8, 1.5 wt%) of $NaH_2PO_4{\cdot}2H_2O$, in air 1300 and 1400 °C for 15 h have been characterized in terms of whisker morphology, composition and structure. Relatively uniform whisker shaped crystals grew within the silicate glass matrix. After chemically leaching the glass matrix with HF solution using a microwave heating source, the resulting whiskers were exposed as isolated crystals and exhibited an aspect ratio of >17 (~0.5 μm in diameter). The mullite whiskers had a composition of 51.06 mol% Al_2O_3 and 48.94 mol% SiO_2, with an orthorhombic crystallographic structure.

Keywords: A. Calcination; B. Whiskers; D. Mullite; E. Structural applications

1. Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) is an attractive potential engineering ceramic because it has high strength and high creep resistance at both low and high temperatures, a low thermal expansion coefficient, and good chemical and thermal stability. Whisker shaped mullite has attracted attention as a possible reinforcement for high temperature structural materials. The stable crystal structure of mullite is orthorhombic with lattice constants $a = 7.545$ Å, $b = 7.689$ Å and $c = 2.884$ Å (JCPDS Card # 15-776), and it consists of edge-shared AlO_6 octahedral chains aligned in the *c*-direction and cross-linked by corner-shared $(Si,Al)O_4$ tetrahedra [1]. Thus, the crystal growth may be faster in crystallographic direction parallel to the *c*-axis than in any other, resulting in a high degree of orientation.

Several processing routes have been reported for the preparation of mullite whiskers. Hashimoto and Yamaguchi [2] synthesized mullite whiskers with an aspect ratio of 15–20 and a diameter of 0.5–2 μm, by firing a powder mixture of $Al_2(SO_4)_3$ and amorphous SiO_2 together with Na_2SO_4 flux in an alumina crucible at 1000 °C for 2 h. Choi and Lee [3] obtained very large mullite whiskers (>15 μm in diameter, >300 μm in length) by heating a mixture of SiO_2 and silicon in an alumina tube reactor, under a flow of H_2/CF_4 at 1450 °C for 3 h. Moyer and Hughes [4] formed fluorotopaz by reacting a mixture of alumina and silica with SiF_4 at >600 °C and then produced the large interlocked mullite whiskers (diameter ~100 μm and aspect ratio 10–15) by its subsequent decomposition below 1000 °C. Peng and Sorrell [5] introduced an inexpensive, simple method for preparation of mullite whiskers with an average length of 100 μm; the thermal decomposition of natural topaz with the addition of 0.5 wt% AlF_3 was done at 1300 °C for 4 h with and without flowing air. Hong et al. [6] investigated anisotropic grain growth of B_2O_3-doped mullite which was seeded with mullite whiskers; after firing at 1650 °C for 5 h, a system seeded with 2 wt% mullite whiskers and doped with 2 wt% B_2O_3, exhibited the largest anisotropic grains with an aspect ratio of >10 and a length of >30 μm. Perera and Otsuka [7] synthesized mullite whiskers with an aspect ratio of 3–8 (0.5–5 μm in length) by the simple process of firing kaolin minerals at 1400–1600 °C.

More recently, Li et al. [8] prepared short mullite fibers by adapting the kneading–drying–calcination (KDC) process and examined the effect of foaming agent on the formation of mullite fiber from kaolin. They reported that the addition of 10 wt% sodium dihydrogen phosphate followed by calcination at 1500 °C for 10 h, promoted the growth of mullite fiber (aspect ratio ~28, diameter ~1.0 μm) and reduced the treatment time (3 h) required for dissolution of the glass matrix in 20 wt% HF solution. They also noted that the addition

* Corresponding author. Tel.: +82 51 510 2392; fax: +82 51 512 0528.
E-mail address: hcpark1@pusan.ac.kr (H.C. Park).

0272-8842/$34.00
doi:10.1016/j.ceramint.2008.01.017

of 10 wt% sodium dihydrogen phosphate caused a sudden reduction (~41%) in yield of mullite, compared with 2 wt%. However, except for noting the effect of an addition of sodium phosphate to kaolin to aid the fabrication of short mullite fibers, the authors gave no detailed data concerning the composition or structure of their mullite fibers.

In the fabrication of mullite whiskers by solid-state reaction in the presence of a liquid phase, it is difficult to dissolve effectively the glass matrix which forms around the whiskers, even though a solution of HF in water is used. In such cases, a highly concentrated leaching solution and/or a prolonged leaching time can also dissolve the whisker phase formed in the reaction. Microwave-assisted leaching techniques can be used to remove the glass matrix rather more easily due to the inherent advantages of microwave energy being selective [9].

In the present work, a similar method to that of Li et al. [8] has been applied to obtain mullite whiskers from kaolin; however, different processing conditions designed to be more economical and less destructive to the natural environment have been employed. At the same time the key objective of this study has been to further understand the effect of fundamental factors underlying the development of mullite whiskers from kaolin, and to characterize the whiskers formed.

2. Experimental procedure

A commercial-grade kaolin with a Al_2O_3/SiO_2 molar ratio of 0.13, $NH_4Al(SO_4)_2{\cdot}12H_2O$ (purity >99.9%) obtained from coal fly ash [10] and reagent-grade $NaH_2PO_4{\cdot}2H_2O$ (Junsei Chemical Co., Tokyo, Japan) have been used as starting materials. The kaolin was calcined in air at 800 °C for 2 h to increase its reactivity; it was subsequently ball-milled in ethanol for 24 h using a polyethylene bottle with alumina ball media. After rotary vacuum evaporation (R-114, Buchi, Switzerland), the dried powder was ground in an agate mortar and passed through a 200 mesh nylon sieve. A measured amount of $NH_4Al(SO_4)_2{\cdot}12H_2O$ was added to the kaolin in order to increase the Al_2O_3/SiO_2 molar ratio to 0.51. In addition, 0.8 and 1.5 wt% $NaH_2PO_4{\cdot}2H_2O$ were added to the mixture of kaolin and $NH_4Al(SO_4)_2{\cdot}12H_2O$. The starting batch composition was selected with reference to the literature of Li et al. [8]. The batch powders were mixed and homogenized by ball milling in ethanol for 8 h using a high density polyethylene bottle with alumina ball media. After drying, the mixed powders were crushed in an agate mortar and passed through a 200 mesh sieve. Cylindrical (10 mm diameter × 5 mm) compacts were prepared by die pressing at 70 MPa. The compacts were placed in an alumina crucible and calcined at 1300 and 1400 °C for 15 h. The calcined compacts were treated with 5–15 wt% HF solution in water; the product was filtered, washed with water, and finally dried. In this case, in order to effectively dissolve the glass matrix from the whiskers, the HF solution was heated at 50 °C for 1–3 h using a microwave heating source (2.45 GHz, 3 kW, Hankuk Microwave Co. Korea).

The resulting whiskers were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM).

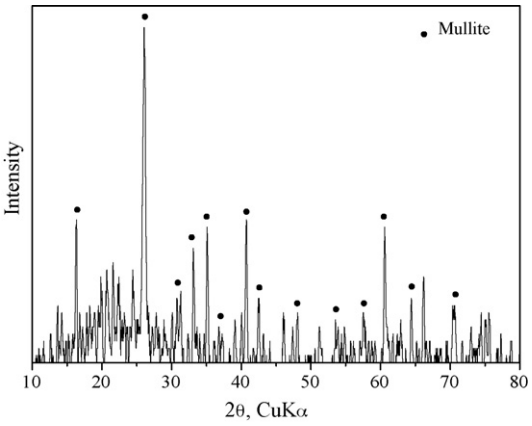

Fig. 1. XRD patterns of the product obtained with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$, fired at 1300 °C for 15 h; they coincided well with those of mullite (JCPDS Card #15-776).

3. Results

XRD analysis showed the product obtained at 1300 °C for 15 h to generate characteristic XRD peaks nearly all which corresponded to mullite (Fig. 1). The product had a relatively uniform microstructure (Fig. 2); it consisted of whiskers seen to have grown within the glass matrix. After chemically leaching the glass matrix with a 5 wt% HF solution using microwave heating (50 °C, 1 h), short mullite whiskers with an aspect ratio of <7 (~0.15 μm in diameter) (Fig. 3(a)) were obtained. They were oriented to a favorable growth direction in specific domains (Fig. 3(b)). As shown in Fig. 4, the growth of the mullite into whiskers increased further (<10 in aspect ratio, 0.5–0.7 μm in diameter) on firing at 1400 °C. At this higher temperature, the preferential orientation of the whiskers was not as apparent. The subsequent leaching, using 10 wt% HF in water, resulted in more unattached and less aggregated whiskers compared with 5 wt% HF solution. The EDS analysis spectrum of the whiskers confirmed that they consisted of

Fig. 2. SEM micrograph of the product obtained with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$; fired at 1300 °C for 15 h; without chemically leaching.

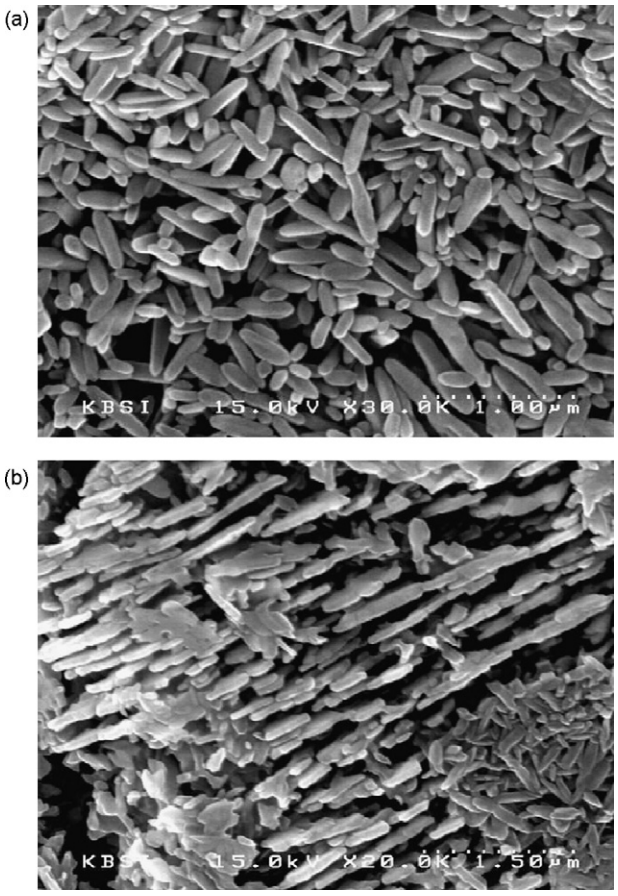

Fig. 3. SEM micrographs of the product obtained with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$; fired at 1300 °C for 15 h; leached by 5 wt% HF solution at 50 °C for 1 h using microwave heating source; showing (a) random orientation and (b) preferential orientation, of the whiskers.

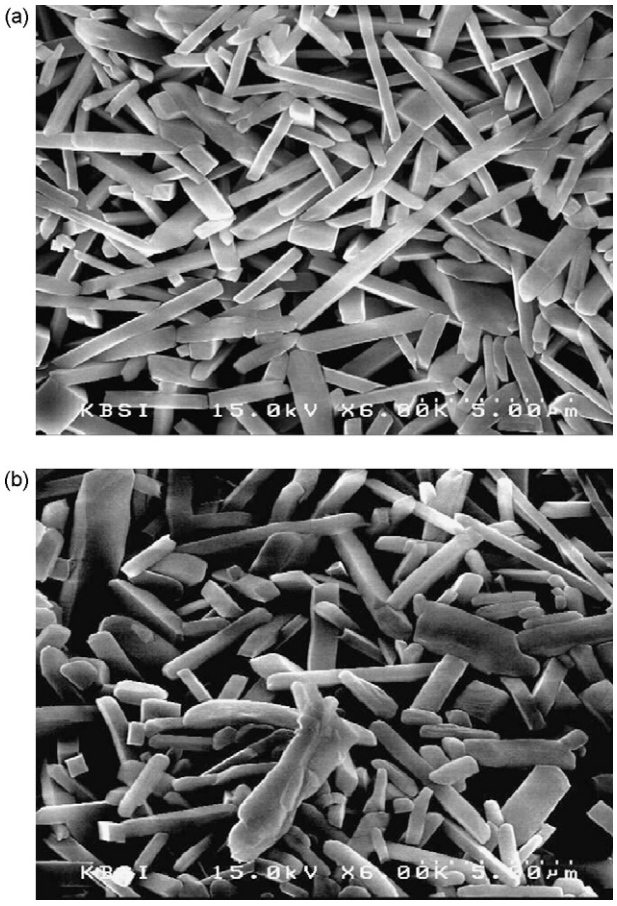

Fig. 4. SEM micrographs of the product obtained with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$; fired 1400 °C for 15 h; leached by (a) 5 wt% and (b) 10 wt% HF solution at 50 °C for 1 h using microwave heating.

63.59 wt% Al_2O_3 and 36.41 wt% SiO_2 (Al_2O_3/SiO_2 = 1.04, molar ratio) (Fig. 5), this result indicating an alumina deficient composition with respect to stoichiometric mullite (Al_2O_3/SiO_2 = 1.5, molar ratio). The crystal structure of the whiskers with a nanometer-sized diameter (~300 nm) was confirmed to be orthorhombic (Fig. 6).

After conventional leaching at 50 °C for 5 h, the microstructure of the product obtained by firing the compact with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$, at 1400 °C for 15, is shown in Fig. 7. Relatively well developed mullite whiskers with an aspect ratio of >12 (0.4–0.6 μm in diameter) were observed, and almost all the glass phase had been dissolved. The prolonged leaching time and/or using a high concentration HF solution also appeared to dissolve the fine whiskers, the relatively coarse ones remaining undissolved, regardless of leaching source (Figs. 4, 7 and 8).

4. Discussion

The growth of mullite into whiskers occurs on firing above the eutectic temperature in the Al_2O_3–SiO_2 system; in such case, it is favorable in the presence of a considerable amount of liquid phase with a high-SiO_2 composition. The impurity content of as-received kaolin measured by XRF was 1.123 K_2O, 0.136 Na_2O, 0.154 CaO, 0.014 MgO, 0.008 P_2O_5, and 0.104 wt% TiO_2; such components, together with the addition of $NaH_2PO_4{\cdot}2H_2O$ contribute to the formation of low melting point in the Al_2O_3–SiO_2 system and relatively low viscosity liquids during firing. The presence of such impurity oxides, especially K_2O and Na_2O, enhances the volume fraction of glassy phase present at any given temperature. It is worth noting that the ternary of Na_2O–K_2O–SiO_2 has a lowest melting point of 540 °C [11] and the introduction of glass-forming oxides

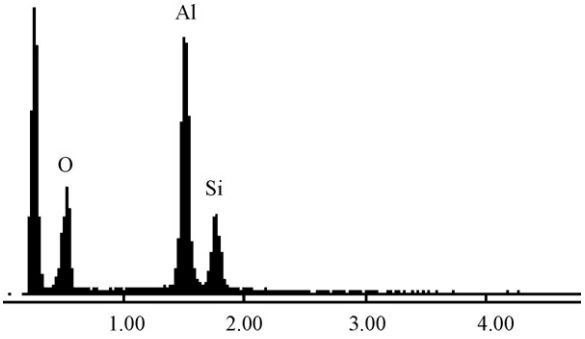

Fig. 5. EDS spectrum of mullite whiskers obtained with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$ and heat treated at 1400 °C for 15 h. Accordingly, the whiskers have the following chemical composition (wt%): 44.14 O, 37.11 Al and 18.75 Si.

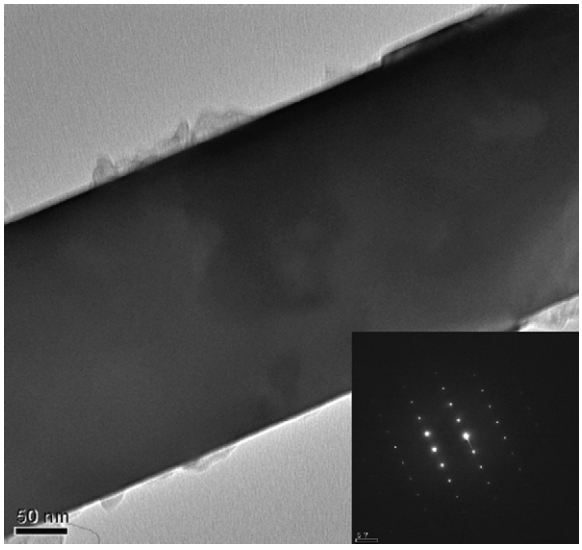

Fig. 6. TEM micrograph and microbeam diffraction of mullite whisker with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$; fired at 1400 °C for 15 h.

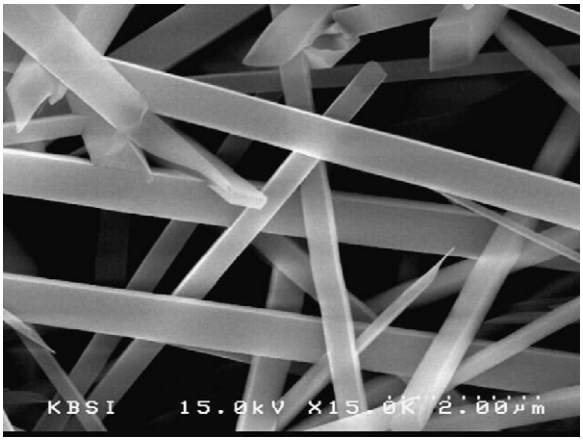

Fig. 7. SEM micrograph of the product obtained with an addition of 0.8 wt% $NaH_2PO_4{\cdot}2H_2O$; fired at 1400 °C for 15 h; leached by 5 wt% HF solution at 50 °C for 5 h using conventional heating.

such as B_2O_3 and P_2O_5 can reduce the viscosity of silicate melts. Thus, the glass phase rich in low melting components will have a lower eutectic temperature and a reduced viscosity. The low viscosity is accompanied by a higher reaction rate with other phases at the glass/solid phase boundary, due to the more rapid removal and replenishment of the reaction species. Thus the development of the mullite whiskers can be explained on the enhanced formation and lower melting point of the secondary glass phase, its presence allowing enhanced solution-precipitation [12,13] of the mullite crystals in the liquid glass matrix.

As shown in Fig. 8, the addition of 1.5 wt% $NaH_2PO_4{\cdot}2H_2O$ resulted in small amounts of enhanced the growth of whiskers with an aspect ratio of >17 (~0.5 μm in diameter), possibly due to the formation of more liquid phase and the lower viscosity of the melt, compared with the addition of 0.8 wt% (Fig. 4). Fahrenholtz and Smith [14] reported that Na_2O did not enhance the crystallization kinetics of mullite but increased the grain size; the grain morphology changed from equiaxed to

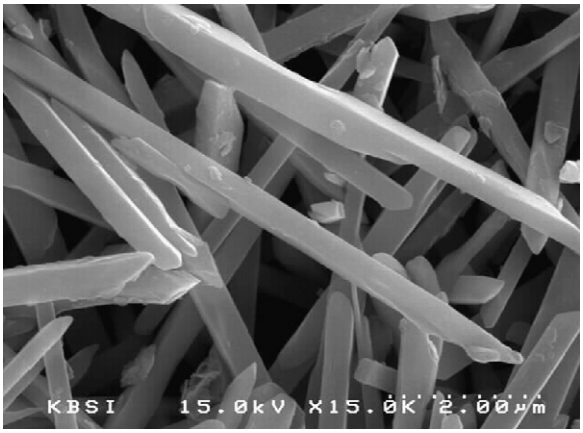

Fig. 8. SEM micrograph of the product obtained with an addition of 1.5 wt% $NaH_2PO_4{\cdot}2H_2O$; fired at 1400 °C for 15 h; leached by 5 wt% HF solution at 50 °C for 3 h using microwave heating source.

anisotropic with increasing Na_2O content. Li et al. [8] considered that the presence of Na_2O caused more glass formation and that P_2O_5 was beneficial for the growth of mullite fibers. On the other hand, Johnson and Pask [15] found that the addition of alkali oxides did not have a great influence on the growth rate of mullite in spite of their strong fluxing effect on Al_2O_3–SiO_2 mixtures. The presence of certain oxides in the glass phase can have a distinctive effect on the morphology of the mullite. Kong et al. [13] investigated the effect of additions of MgO, CaO, SrO, and BaO on the reaction and morphology of the product. Only in the case of MgO addition well developed mullite whiskers formed, the other oxides aided the formation of more plate-like grains. As a consequence, it is assumed that the higher aspect ratio of the whiskers obtained by the addition of 1.5 wt% $NaH_2PO_4{\cdot}2H_2O$ is due to the presence of relatively high concentration of Na_2O and P_2O_5 in the glassy melts, producing larger volume fractions of low viscosity glass which acts as the solvent to the mullite and its precursor oxides. For the same reason, smaller amounts of whiskers tend to be formed with the addition of 1.5 wt% $NaH_2PO_4{\cdot}2H_2O$ compared with 0.8 wt%. In addition, there could well be a poisoning effect on the certain crystallographic planes, inhibiting the growth on these particular planes and allowing the preferential growth on planes perpendicular or close to perpendicular to the long axis of the mullite whisker crystals. Such a process generates the high aspect whisker morphology observed in the present work.

The structure of mullite can have any composition theoretically between $x = 0$ (disordered sillimanite) and $x = 1.00$ (aluminum oxide) in general formula $Al_{4+2x}Si_{2-2x}O_{10-x}$ [16], dependant on starting material and processing route. As a result of this study, the orthorhombic type mullite whiskers, which have a composition 51.06 mol% Al_2O_3 and 48.94 mol% SiO_2 were fabricated using SiO_2-rich starting composition ($Al_2O_3/SiO_2 = 0.51$, molar ratio). The reason is not obvious why the composition of the resulting whiskers is limited to a molar ratio of $Al_2O_3/SiO_2 = 1.04$, but it could be due to limitations of the crystal chemistry of mullite. Another possible reason could well be the low Al_2O_3 content in

the starting batch composition compared with 3/2-mullite, resulting in an Al_2O_3-unsaturated, SiO_2-rich melt. de Souza et al. [17] study mullite whiskers and anisotropic grains derived from 3 mol% erbia-doped aluminum hydroxide and silica gel; the compacts were fired at 1600 °C for 1–8 h. The average molar ratio of Al_2O_3/SiO_2 in the whiskers was 1.31, regardless of the $Al_2O_3/SiO_2 = 1.5$ or 2, molar ratio of the starting composition; in this case a relatively high Al_2O_3/SiO_2 ratio in the glass phase generated a low ratio value in the mullite grains.

5. Conclusions

Relatively well developed whisker-shaped mullite can be prepared by calcining at 1400 °C for 15 h in air of appropriate mixture of fine particle kaolin and $NH_4Al(SO_4)_2{\cdot}12H_2O$ powders, with the addition of 1.5 wt% $NaH_2PO_4{\cdot}2H_2O$. During firing, the whiskers continue to grow into the melts by a solution-precipitation until they impinge; in such case, the whiskers grow preferentially along the parallel direction to the *c*-axis, this resulting in an orthorhombic-type crystallographic structure. The presence of a considerable amount of glass melt could well induce crystal growth on the lateral crystal faces where the free energy difference is not so large. The addition of $NaH_2PO_4{\cdot}2H_2O$ in this respect appeared to be responsible for the development of whisker shaped morphology, possibly due to the further formation of low melting point liquids with low viscosity in the Al_2O_3–SiO_2 system during firing. The leaching of the glass phase by 5 wt% HF in water is more effective using microwave heating source rather than conventional heating.

Acknowledgement

This work was supported financially by the Korea Energy Management Corporation (Project number: 2005-R-NM03-P02) and partially supported by grants-in-aid for the National Core Research Center Program from MOST/KOSEF (No. R15-2006-022-01001-0).

References

[1] J.Y. Jaaski, H.U. Nissen, Investigation of superstructures in mullite by high resolution microscopy and electron diffraction, Phys. Chem. Miner. 10 (1983) 47–54.
[2] S. Hashimoto, A. Yamaguchi, Synthesis of mullite whiskers using Na_2SO_4 flux, J. Ceram. Soc. Jpn. 112 (2004) 104–109.
[3] H.J. Choi, J.G. Lee, Synthesis of mullite whiskers, J. Am. Ceram. Soc. 85 (2002) 481–483.
[4] J.R. Moyer, N.N. Hughes, A catalytic for mullite whiskers, J. Am. Ceram. Soc. 77 (1994) 1083–1086.
[5] P. Peng, C. Sorrell, Preparation of mullite whiskers from topaz decomposition, Mater. Lett. 58 (2004) 1288–1291.
[6] S.H. Hong, W. Germignani, G.L. Messing, Anisotropic grain growth in seeded and B_2O_3-doped diphasic mullite gels, J. Eur. Ceram. Soc. 16 (1996) 133–141.
[7] D.S. Perera, N. Otsuka, Mullite morphology in fired kaolinite/halloysite clays, J. Mater. Sci. Lett. 4 (1985) 1270–1272.
[8] K. Li, T. Shimizu, K. Igarashi, Preparation of short mullite fibers from kaolin via the addition of foaming agents, J. Am. Ceram. Soc. 84 (2001) 497–503.
[9] I.J. Chabinsky, Application of microwave energy past, present and future, in: W.H. Sutton, M.H. Brooks, I.J. Chambinsky (Eds.), Microwave Processing of Materials, Materials Research Society, Pittsburgh, 1988, pp. 17–29.
[10] H.C. Park, Y.J. Park, R. Stevens, Synthesis of alumina from high purity derived from coal fly ash, Mater. Sci. Eng. A 367 (2004) 166–170.
[11] E.M. Levin, C.R. Robbins, H.F. Mcmurdie, Phase Diagrams for Ceramists, vol. 1, The American Ceramic Society, USA, 1964.
[12] M. Bartsch, B. Saruhan, M. Schmucker, H. Schneider, Novel low-temperature processing route of dense mullite ceramics by reaction sintering of amorphous SiO_2-coated γ-Al_2O_3 particle nanocomposites, J. Am. Ceram. Soc. 82 (1999) 1388–1392.
[13] L.B. Kong, Y.Z. Chen, T.S. Zhang, J. Ma, F. Boey, H. Huang, Effects of alkaline-earth oxides on phase formation and morphology development of mullite ceramics, Ceram. Int. 30 (2004) 1319–1323.
[14] W.G. Fahrenholtz, D.M. Smith, Densification and microstructure of sodium-doped colloidal mullite, J. Am. Ceram. Soc. 77 (1994) 1377–1380.
[15] S. Johnson, J.A. Pask, Role of impurities on formation of mullite from kaolinite and Al_2O_3–SiO_2 mixtures, Am. Ceram. Soc. Bull. 61 (1982) 838–842.
[16] C.W. Burnham, Composition limits of mullite and the sillimanite-mullite solid solution problem, Carnegie Inst. Washington Year Book 63 (1964) 227–228.
[17] M.F. de Souza, J. Yamamoto, I. Regiani, C.O. Paiva-Santos, D.P.F. de Souza, Mullite whiskers grown from erbia-doped aluminum hydroxide-silica gel, J. Am. Ceram. Soc. 83 (2000) 60–64.