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A novel processing route for whisker shaped mullite-alumina composites from kaolin

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Whisker shaped mullite/particulate alumina composites prepared by a two-step *in situ* processing route have been characterized in terms of their microstructure and mechanical properties. Well-developed mullite whiskers were firstly formed at 1300 °C for 15 h and subsequently sintered at higher temperatures (≤ 1650 °C). A liquid phase was formed by the reaction of SiO₂ and Al₂O₃, aided by the presence of Na₂O and P₂O₅; these additions improved the formation and growth of mullite whiskers. The mechanical properties of the sintered materials appeared to be mainly governed by the grain size of the major phase, the presence of voids, and an intergranular glass.

Key words: Whisker shaped mullite/particulate alumina composites, In situ processing, Kaolin, Foaming agent.

Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$), because of its high melting point, chemical stability, good thermal and mechanical properties, is a major constituent of tiles, porcelains, structural clay and refractory 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 AlO₆ octahedral chains aligned in the c-direction and crosslinked by corner-shared (Si,Al)O₄ tetrahedra [1]. Thus, the crystal growth may be faster in the crystallographic direction parallel to the c-axis than in any other, resulting in a high degree of orientation.

Whisker-shaped mullite has attracted attention because of its attractive properties as a reinforcement phase for toughened ceramic composites. Mullite whiskers can be easily obtained from clay minerals with the addition of liquid forming agents by firing at 1200-1500 °C [2]. However, it is very difficult to leach the glass matrix effectively from the whiskers once formed. The objective of the present study is to develop an in situ processing route of whisker shaped mullite/alumina composites from kaolin for light weight building materials with improved mechanical properties. The Al₂O₃/SiO₂ molar ratio was controlled by adding alumina to kaolin and a small amount of foaming agent was also introduced. The compacts were heated at 1300 °C for 15 h to form mullite whiskers and then sintered at ≤ 1650 °C. The effects of processing variables on the sintered microstructure and mechanical properties are discussed.

Experimental Procedure

The as-received kaolin with an Al₂O₃/SiO₂ molar ratio of 0.13 was calcined in air at 800 °C for 2 h to increase its reactivity; it was subsequently ball-milled in ethanol for 24 h, rotary vacuum evaporated, ground, and passed through a 200 mesh nylon sieve. A measured quantity of alumina (AES-11C, Sumitomo Chemical Co.) was added to the mixture of 45.1 wt% kaolin and 54.9 wt% NH₄Al(SO₄)₂·12H₂O to adjust the Al₂O₃/SiO₂ molar ratio to 1.8 (specimen 'A'), 1.5 ('B') and 1.2 ('C'). In addition, 2 wt% of sodium dihydrogen phosphate (NaH₂PO₄ · 2H₂O, Junsei Chemical Co.) was introduced. Each of the batch powders were mixed and homogenized by ball milling in ethanol for 8 h using a high density polyethylene bottle with an alumina ball media. After drying, the mixed powders were crushed in an agate mortar and passed through a 200 mesh sieve.

Cylindrical (10 mm dia. \times 5 mm) and rectangular (10 mm \times 10 mm \times 50 mm) compacts were prepared by die pressing under 70 MPa, and then cold isostatic pressing under 200 MPa. After calcining the compacts at 800 °C for 1 h with a heating rate of 2 °C minute⁻¹ to prevent cracking at high temperature, preliminary heating was carried out at 1300 °C for 15 h to develop whisker-shaped mullite crystals and then densification was achieved by maintaining at the sintering temperature (1650 °C) for 2 h.

The sintered bulk density was measured by the water immersion method. Crystalline phases were identified by XRD (D-MAX 1400, Rigaku). The sintered, polished and fracture surfaces were examined using SEM (JSM-840A, Jeol). The four point bend strength was measured using a Universal Test Machine (KSU-5M, Kyung Sung Testing Machine Co.) with a constant crosshead speed of 0.5 mm minute⁻¹, a supporting span of 30 mm, and a

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loading span of 10 mm. The compression strength was calculated using the appropriate equation for the diametral compression disc test [3]. Fracture toughness was evaluated by the indentation technique (136° Vickers indenter, 10 kg, 10 s) [4].



Fig. 1. XRD diffraction patterns of (a) specimen 'A', (b) 'B' and (c) 'C' sintered at $1500 \text{ }^{\circ}\text{C}$ for 2 h.

Table 1. Apparent bulk density, open porosity and water absorption of sintered specimens



Fig. 2. Resolution of the 120/210 peak of mullite in specimen 'C' sintered at (a) 1500, (b) 1600, and (c) 1650 °C for 2 h.

Results and Discussion

XRD patterns for specimen 'A', 'B' and 'C' sintered at 1500 °C for 2 h are shown in Fig. 1, similar XRD patterns were also obtained by sintering at 1600 and 1650 °C. The sintered specimens exhibited XRD patterns consisting of the characteristic peaks of mullite and α -Al₂O₃; in such a case, the peak intensities of the minor phase of α -Al₂O₃ slightly increased with increasing Al₂O₃/SiO₂ molar ratio, independent of sintering temperature. It is presumed that the presence of the α -Al₂O₃ phase is due to the formation of a binary and/or a ternary low melting point liquid which contains a considerable amount of SiO₂ leaving an insufficient quantity of SiO₂ precipitated to react with all of the remaining Al₂O₃ present at the firing temperature. The XRD peak lines of mullite were shifted to higher 2θ -values compared with the JCPDS card #15-776. The reason is not obvious but could be due to the formation of a solid solution together with minor impurity components, these being of smaller ionic size compared with Al³⁺ (0.57 Å) and Si⁴⁺ (0.39 Å). Another possible reason could well be the low Al₂O₃ content in the starting batch composition compared with 3/2-mullite. As shown in Fig. 2, from the XRD measured at a low scanning speed (0.25°/minute), there was angular separation of the reflection

Specimen	Sintering temperature (°C)	Apparent bulk density (g/cm ³)	Open porosity (%)	Water absorption (%)
	1500	2.74	8.0	2.9
А	1600	2.66	11.5	4.4
	1650	2.71	8.3	3.1
В	1500	2.88	0.7	0.2
	1600	2.74	1.1	0.4
	1650	2.59	1.3	0.5
С	1500	2.76	1.6	0.6
	1600	2.43	1.0	0.4
	1650	2.13	4.6	2.2

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Fig. 3. SEM micrographs of an inner surface of specimen 'C' sintered at 1650 $^{\circ}\mathrm{C}$ for 2 h.

pair (120)/(210) around 26° (2 θ), indicating the crystal growth of mullite in an orthorhombic structural form. With increasing firing temperature, the angular separation became more evident with increased XRD peak intensities, this indicating the presence of well-developed mullite crystals [5].

Owing to the slowness of the diffusion of Al^{3+} and Si^{4+} species, mullite is not easily sintered; in such a case, the presence of impurities in kaolin and with addition of $NaH_2PO_4 \cdot 2H_2O$, these factors may induce liquid phase sintering, resulting in improved densification.

The effects of batch composition and sintering temperature on the physical properties of mixed powder compacts are shown in Table 1. The sintered bulk density had a value which was determined to be in the range 67.6-91.5% of the theoretical density of mullite (3.15 g/cm^3) . After sintering at 1650 °C, the bulk densities decreased with an increase of SiO_2 content in the batch composition, possibly due to the presence of increased silica-rich glass phase and voids. On firing, the presence of such a silica-rich melt could induce further growth of mullite crystals (Fig. 3), resulting in the development of residual pores, lined with the mullite crystals, resulting in decreased bulk density. By comparison with sintered bulk density values, relatively low open porosity and water absorption were observed, this implying that almost all the pores present consisted of closed pores sealed by the solidified glass phase.

After sintering at 1500 °C, some coarse pores (2-4 µm)





Fig. 4. SEM micrograph of polished and thermally etched surface of specimen 'A' sintered at (a) 1500 °C and (b) 1600 °C for 2 h.

were mainly dispersed at the grain boundaries of the matrix, regardless of batch composition, but the presence of the pores was more remarkable, especially in the specimen which was Al₂O₃-rich (specimen 'A') (Fig. 4(a)). Generally, with low-Al₂O₃ contents near to that of 3/2-mullite (ca 72 wt% Al₂O₃), the highest densification is obtained, whereas high-Al₂O₃ compositions (> 75 wt% Al₂O₃) exhibit poor densification [6]. With increasing sintering temperature, the pore size decreased together with improved densification (Fig. 4(b)). In the specimens with Al₂O₃/SiO₂, molar ratio = 1.2, sintered at 1650 °C, Al₂O₃ inclusions were located near the grain boundaries of the matrix, and small spherical Al₂O₃ (< 0.3 µm) particles, the shape being typical



Fig. 5. SEM micrograph of polished and thermally-etched surface of specimen 'C' sintered at 1650 °C for 2 h.

Specimen	Sintering temperature (°C)	Radial compression strength (MPa)	Bend strength (MPa)	Toughness (MPa · m ^{1/2})
А	1500	168.9 ± 27.5	86.6 ± 19.3	-
	1600	387.1 ± 48.3	104.6 ± 6.5	7.9 ± 1.4
	1650	194.8 ± 86.6	110.2 ± 13.1	-
В	1500	176.1 ± 49.3	87.4 ± 13.5	8.4 ± 0.2
	1600	196.3 ± 45.3	94.2 ± 8.8	7.8 ± 1.6
	1650	175.3 ± 46.3	85.4 ± 11.0	-
С	1500	190.6 ± 38.1	103.8 ± 2.1	7.7 ± 0.6
	1600	215.8 ± 80.1	69.5 ± 6.8	-
	1650	143.3 ± 66.6	48.9 ± 24.5	-

Table 2. Radial compression strength, bend strength and fracture toughness of sintered specimens

of a crystal wetted by a surrounding glass phase, were dispersed within the mullite grains (Fig. 5). Growth of mullite into whisker-shaped crystals was most prevalent in the specimens with a low Al_2O_3 composition. From this fact, it was concluded that (i) on firing at 1300 °C for 15 h, the presence of a significant amount of SiO₂-rich melt could enhance the development of mullite into whiskers; (ii) with further firing at higher temperatures (≤ 1650 °C), the whiskers were interlocked with each other, and indeed had undergone significant intergrowth.

The diametral compression strength, four point bend strength, and fracture toughness of sintered materials are shown in Table 2. The specimens sintered at 1600 °C exhibited superior compression strength regardless of the starting batch composition; the 3/2-mullite composition had the highest value recorded, 387 MPa. On the other hand, for the same starting composition, the specimens sintered at 1650 °C showed relatively low strength, presumably due to the exaggerated grain growth of the mullite phase. The typical fracture pattern of the 1600 °C-sintered specimens with relatively high strength values was similar to a triple-cleft mode [7].

Specimen 'A' sintered at 1650 °C, consisting of relatively short whiskers, had a high bend strength of ~110 MPa, compared with those of materials prepared in different conditions. The extrusion of liquid phase onto the surface and also bloating phenomenon occurring in this processing, greatly lowered the strength of specimen 'C' especially when sintered at 1650 °C. In this study, however, the dependency of sintering temperature and batch composition on bend strength was not generally consistent. The sintered specimens had high values of toughness, 7.7-8.4 MPa \cdot m^{1/2}. However, for the specimens prepared with some processing conditions, the toughness could not be reliably measured because the pores were dispersed in a wider range and therefore the lengths of indentation cracks induced at 98 N were not optically clear. Micro-fracture with grain bridging and crack bridging was observed, and inter-granular fracture and crack deflection by secondary particles can be seen (Fig. 6). Fig. 7 shows the microstructures of fracture surfaces of specimens having different batch compositions, all sintered at 1600 °C. Intergranular fracture mainly occurred through the glass phase.

Conclusions

Two-phase, low density, mullite whisker/alumina particulate composite materials can be prepared by the controlled in situ processing of batches with Al₂O₃/SiO₂ molar ratios of 1.8, 1.5 and 1.2, and with the addition of 2 wt% of NaH₂PO₄ · 2H₂O. The apparent bulk density, open porosity and absorption water of the composites were 2.13-2.88 g/cm³, 0.7-11.5% and 0.2-4.4%, respectively. The specimens with Al₂O₃/SiO₂ molar ratios of 1.5 and 1.2 formed relatively well-developed mullite whiskers, compared with the alumina-rich composition. According to the processing conditions, the sintered materials showed a widely ranged radial compression strength (143-387 MPa) and bending strength (49-110 MPa). The presence of voids and glass phase was considered as a main cause of the lower values measured, the voids providing large flaws and the glass phase reducing the fracture toughness.



Fig. 6. Crack profile induced by Vickers indentation (98 N) in specimen 'B' sintered at 1500 °C for 2 h.







(c)

Fig. 7. SEM micrographs of fracture surfaces of specimens (a) 'A', (b) 'B', and 'C' sintered at 1600 °C for 2 h.

The mullite whiskers which were developed below the normal sintering temperatures appeared to be responsible for a more marked increase of fracture toughness (7.7- $8.4 \text{ MPa} \cdot \text{m}^{1/2}$) of the sintered materials. However, in order to obtain high toughness, enhanced microstructural reliability is required. The fracture path of the sintered materials proceeds mainly through the glass phase at the crystal boundaries.

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