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Influence of raw material type and of the overall chemical composition on phase formation and sintered microstructure of mullite aggregates

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Abstract

Dense mullite aggregates with varied (47–70%) alumina contents have been prepared by a conventional dry-powder pressing technique followed by heat treatments at temperatures in the range of 1450–1725 °C. Different types of clays, beach sand sillimanite (BSS) and a high purity aluminium hydroxide were used as starting materials. Mullites derived from BSS consisted of equi-axed grains whereas those obtained from clay containing precursor mixtures exhibited elongated grains. The bulk density (BD), apparent porosity (AP) and water absorption (WA) capacity of sintered mullites were found to be strongly influenced by the pre-mullitization step of the precursors and in a less extent by the type of raw material, its hydration degree and the impurity contents of Fe_2O_3, CaO and Na_2O. Mullite aggregates obtained from the three different types of aluminosilicate raw materials (i.e., ball clay, china clay and beach sand sillimanite) through a double-stage heat treatment process exhibited better sintered properties in terms of bulk density, apparent porosity, water absorption capacity and higher mullite contents in comparison to those obtained following a single-stage firing process.

Keywords: D. Mullite; Ball clay; China clay; Beach sand sillimanite; Double-stage firing process

1. Introduction

Mullite is known for its several important properties such as, good chemical inertness, low thermal conductivity, high creep resistance, high refractoriness and low thermal expansion coefficient [1–5]. For most applications, mullite is synthetically made following various routes, with predominance of reaction sintering from alumina and silica precursors. The stable composition range of mullite in the Al_2O_3–SiO_2 system is ≅70.5–74 wt.% Al_2O_3, and its theoretical density varies between 3160 and 3220 kg/m^3. The stoichiometric mullite $3Al_2O_3{\cdot}2SiO_2$ corresponds to 71.8 wt.% alumina [3]. The performance of refractory materials based on mullite, is governed by chemical composition, which usually contain 47–70 wt.% Al_2O_3 [4], and by the sintered microstructure. Fused mullite or sintered mullite with low grain boundary populations and relatively large size (>40 μm) equi-axed grains are preferred for refractory applications due to their relatively high resistance to attack by the slag [6]. The morphology of mullite grains derived from silica-rich compositions is needle-like, whereas that from alumina-rich compositions is more equi-axed. The evolution of mullite microstructure is not only influenced by the chemical composition but also by the nature of the starting raw materials [7]. In the case of naturally occurring raw materials, sillimanite group of minerals leads to the formation of mullites with equi-axed grains, whereas kaolinite leads to needle-like grains. However, none of the existing mullite-related articles clearly demonstrated the effects of naturally occurring raw materials and chemical composition on the formation, densification behaviour and sintered microstructure [8,9]. Normally, cheap, readily and abundantly available high purity natural raw materials like kaolinite, sillimanite, ball clay, bauxite (gibbsite and diaspore) and halloysite are preferred for the production of refractory grade mullite aggregates [1–9]. The mullite aggregates formed from these raw materials show a falloff in properties such as, high-temperature strength, corrosion resistance and chemical durability, in proportion to impurity levels [10].

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In this investigation, we have undertaken a systematic study to establish the effects of raw material type and chemical composition on the formation, densification behaviour and sintered microstructure of relatively high purity mullite aggregates formed from abundantly available natural raw materials. For this purpose, mullite-based compositions having 47–70 wt.% alumina were formulated using beach sand sillimanite (BSS), ball clay, china clay and high purity aluminium hydroxide as raw materials. The actual alumina content of stoichiometric mullite varies in the range of 70.5–74 wt.% [3]. The batch formulations were homogenised, compacted by uni-axial dry-powder pressing technique and then heat treated for 1–3 h at temperatures in the range of 1450–1725 °C before and after subjecting to an intermediate calcination treatment at 1250–1300 °C for 1 h. The differently sintered mullites were thoroughly characterized for bulk density (BD), apparent porosity (AP), water absorption (WA) capacity, XRD phase composition and microstructural features in order to understand the relationships between the final properties, the heat treatment schedule, and the characteristics of starting raw materials.

2. Experimental procedure

2.1. Raw materials and powder processing

Commercial ball clay (BC) and china clay (CC) procured from Mysore Minerals Ltd., Bangalore, India, and a beach sand sillimanite (S) from Indian Rare Earth Ltd., Kerala, India, were used as sources of aluminosilicates. A commercial aluminium tri-hydroxide (A) (NALCO, NSPH-10, India) synthesized according to the Bayer process was used as a source of alumina. The physicochemical properties of raw materials as provided by the suppliers are presented in Table 1. For comparison purposes, commercial mullite samples (Mulcoa 47, Mulcoa 60 and Mulcoa 70), procured from M/s. CE Minerals, China, were also used in this study.

In a typical experiment, powder mixtures containing different amounts of alumina and aluminosilicate sources were co-ground for 6 h in a rotary steel jar mill (250 mm diameter and 300 mm height) using steel balls (20 mm diameter) and a balls to charge ratio of 2:1. The ground powders mixtures were converted into granules with sizes <595 μm with the help of an aqueous polyvinyl alcohol (PVA) solution (5 wt.%). Dried granules were pressed uni-axially under 200 MPa pressure into pellets having 30 or 70 mm diameter × 10 mm height. Pressed pellets were then heat treated for 1–3 h in an electrically operated open-air furnace at 1450–1725 °C using a heating rate of 180 °C/h. Some of the raw materials mixtures were subjected to an intermediate calcination process prior to sintering. In this case, ground raw materials mixtures were initially converted into extrudable dough in a Sigma kneader (Frigmayers, India) with the help of 30% aqueous solution containing 3 wt.% dextrin (Loba-Chemie, India) and then extruded into 20 mm diameter rods using a twin-screw horizontal extruder (BB Engineering Works, India). Extrudates were oven dried at 120 °C overnight and calcined for 1 h at 1250–1300 °C under the same conditions reported above to obtain powders with mullite phase contents >60%. All the calcined powders were once again ground for 6 h under the same conditions reported above prior to pressing and final sintering.

2.2. Material characterization

The XRD patterns were recorded on a Bruker (Karlsruhe, Germany) D8 advanced system using diffracted beam monochromated Cu Kα (0.15418 nm) radiation source. Crystalline phases were identified by comparison with Powder Diffraction File (PDF)-4 reference data from International Centre for Diffraction Data (ICDD). Easy Quant, the semi-quantitative feature of JADE software, was used to calculate the weight percent of each identified phase [11,12]. The JADE software uses the peak area information along with the phase RIR (relative intensity ratios). The vitreous phase was disregarded in the XRD analysis because it could not be quantified with the facilities available in our lab. It will be higher in the silica-rich compositions and will enhance the liquid phase diffusion of species, facilitating the earlier formation of mullite and its needle-like morphology. Particle size analysis of powders was determined using a particle size analyzer (Granulometer G 920,

Table 1
Raw materials specifications[a].

Property	Ball clay	China clay	Sillimanite	Aluminium hydroxide
Code given	BC	CC	S	A
Al_2O_3 (wt.%)	34.2	35.16	53.5	64.5
SiO_2 (wt.%)	48.7	49.98	40.1	0.009
ZrO_2 (wt.%)	–	–	2.5	–
CaO (wt.%)	0.28	0.51	0.5	0.03
MgO (wt.%)	0.31	0.22	0.3	–
Fe_2O_3 (wt.%)	1.6	0.65	0.80	0.007
Na_2O (wt.%)	0.21	0.18	0.07	0.23–0.30
K_2O (wt.%)	1.21	0.09	0.2	–
TiO_2 (wt.%)	1.28	1.13	1.3	0.26–0.32
LoI (RT–1000 °C)	12.21	12.08	0.73	34.50
Average particle size (μm)	7.30	5.16	6.32	5.12
Crystalline phases	–	Kaolinite	Sillimanite	γ-Al_2O_3 (>90%); α-Al_2O_3 (<10%)

[a] Provided by the suppliers.