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ScienceDirect
Journal of the European Ceramic Society 31 (2011) 687–695
www.elsevier.com/locate/jeurceramsoc

Sintering and characterization of flyash-based mullite with MgO addition

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Received 29 September 2010; received in revised form 1 December 2010; accepted 7 December 2010
Available online 6 January 2011

Abstract

Mullite ceramics were fabricated at relatively low sintering temperatures (1500–1550 °C) from recycled flyash and bauxite with MgO addition as raw materials. The densification behavior was investigated as function of magnesia content and sintering temperature. The results of thermal analysis, bulk density and pore structure indicate that MgO addition effectively promoted sintering, especially above 1450 °C. Due to the presence of large interlocked elongated mullite crystals above 1450 °C, associated with enhanced densification, an improvement in mechanical strength was obtained for the samples containing magnesia. The addition of magnesia slightly decreases the LTEC at 1300 °C due to the formation of low-expansion α-cordierite, but slightly increases the LTEC above 1400 °C due to the formation of high expansion corundum and $MgAl_2O_4$ spinel.

Keywords: Flyash; Environmental application; Mullite; Sintering; Magnesia

1. Introduction

In recent years, there has been considerable increasing interest in environmental problems worldwide. In particular, many researchers have concentrated more attention on seeking sustainable methods for recycling of hazardous industrial wastes. As an abundant waste, coal flyash is a by-product derived from raw coal combustion in thermal power plants and factories which presents many countries with serious problems of storage and environmental pollution but it can be considered as the world's fifth largest raw material resource.[1] Research activities relating to the utilization of flyash have resulted in various applications, mainly in the construction sector (cement and concrete),[2] agriculture sector (soil amendment) and advanced materials such as mineral polymers, synthetic zeolite, glass, glass–ceramics, porous ceramics and composite catalysts.[3] In many cases, the chemical and phase compositions of flyash are complex, depending on raw coal and combustion conditions.[4] In spite of its diversity, flyash is rich in certain metal oxides such as silica (SiO_2) and alumina (Al_2O_3). This gives flyash the potential to be used as a low cost material source for the glass and ceramic industries. The effective utilization of waste flyash not only resolves a huge environmental issue, but also produces high value-added materials while conserving natural resources.

Mullite is a strong candidate ceramic for advanced structural applications at high temperatures, because it has a high melting point, good creep resistance, superior high temperature strength, exceptional thermal shock resistance and exhibits good chemical stability in harsh chemical environments. Amongst the potential applications are thermal and environmental barrier coatings for aircraft and gas turbine engines, catalytic converters, kiln furniture and hot gas filters/membranes, 3:2 mullite has a highly stable open structure and it can accommodate transition metal cations into its structure.[5] Flyash, in which SiO_2 and Al_2O_3 are its main components, is very suitable to produce mullite because it contains large amounts of reactive SiO_2 and alumina.[6] Recently, some researchers have attempted to prepare mullite from this waste with addition of industrial α-alumina.[7–10] In our previous work,[11] a dense 3:2 mullite was synthesized from flyash with addition of raw bauxite as alumina source. A unique vol-

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doi:10.1016/j.jeurceramsoc.2010.12.012

ume expansion occurred at 1380–1520 °C, resulting in a highly porous microstructure. In order to obtain dense mullite, therefore, it is necessary to commence densification before expansion.

The use of sintering aids is a quite important strategy in reduction of sintering temperatures for pure mullite. Some oxides such as titania, ferric oxide, strontia, ceria and YSZ (yttrium stabilized zirconia) have been very effective in promoting densification.[12–14] MgO has been used as an effective aid to lower sintering temperature of industrial mullite[12,15,16] and combustion processed mullite.[17] Nevertheless, most of the past research has focused on low-temperature densification of pure mullite. Little attention has been paid to the effect of MgO addition on the properties of reaction-sintered mullite made from recycled materials.

In the current work, reaction-sintered 3:2 mullite was prepared from two recycled materials, i.e., waste flyash and natural bauxite, with MgO as sintering aid. The effects of MgO content and sintering temperature on sintering behavior, mechanical and thermal properties, phase composition and microstructure were studied in detail.

2. Experimental procedure

2.1. Starting materials, pressing and sintering

Flyash (Hefei No. 2 thermal power plant, PR China) and natural bauxite (Yangquan City, PR China) powders were used as the main starting materials to prepare mineral-based mullite.[11] Basic magnesium carbonate (AR; $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$; Sinopharm Chemical Reagent Co., Ltd.) was used as the magnesia source for the sintering additive. The mixture of flyash and bauxite, based on the composition of 3:2 mullite (W_{flyash}:$W_{bauxite}$ = 45.87:100), was wet-mixed for 6 h using zirconia balls with distilled water as medium in a polyethylene pot. The average particle diameters of flyash, bauxite and their mixture are 1.76, 1.13 and 1.52 μm. For the mixture, most of the particles center at 1.00–4.00 μm in diameter.

After wet-mixing, basic magnesium carbonate was added and the agitation was continued unceasingly for 2 h using a mechanical stirrer. Then, the slurry of mixed powders was completely dried at 120 °C. Afterwards, the mixture was slightly crushed to break the agglomerates, mixed with binder PVA-1750 (5.00 wt.%) and then uniaxially pressed at 160 MPa. Both rectangular bars (50 mm × 6 mm × 3–4 mm) and cylindrical pellets (25 mm in diameter; 2–3 mm in height) were made. After sufficient drying at 120 °C, the samples were fired between 1300 and 1500 °C at intervals of 50 °C for 2 h dwelling time. The heating rates were 1 °C min^{-1} from room temperature to 450 °C, 2 °C min^{-1} from 450 to 650 °C, and 3 °C min^{-1} from 650 °C to the final firing temperatures. A dwelling time of 1 h was carried out at 450 and 650 °C, respectively, to remove added organic additives and inherent structural water in natural bauxite.

2.2. Characterization techniques

The particle size distributions of flyash, bauxite and their mixture were determined using a laser particle size analyzer (Rise-2006, Jinan Rise Science & Technology Co. Ltd., PR China) using PEG-10000 (polyethylene glycol; molecular weight: 10,000 g mol^{-1}) as dispersing agent. Sintering shrinkage behavior of the green bodies containing various magnesia contents was measured between 26 °C and 1550 °C at a heating rate of 3 °C min^{-1} in a horizontal dilatometer (DIL 402C, Netzsch, Germany).

Linear dimensional changes in the diameters of the sintered pellets were measured using a vernier caliper. In addition, both bulk density and open porosity were measured in distilled water using the Archimedes' replacement method. Pore size distributions were examined in a lab-made equipment according to the bubble point method, which is on the basis of gas–liquid replacement mechanism.[18]

Room temperature flexural strength was determined by the three-point bending method in a universal materials testing machine (3369, Instron Corporation, USA). A span length of 30 mm and crosshead speed of 0.5 mm min^{-1} were used. All the tested bars were polished and beveled in advance by 360-mesh and then 800-mesh metallographic sandpapers in order to eliminate surface stress. Fracture strength was calculated according to the following expression (ISO9693 1999).

$$\sigma = \frac{3P \times l}{2b \times h^2}$$

where σ is fracture strength (Pa), P is fracture load (N), l is span length (m), b is sample width (m), h is sample height (m).

Fracture surfaces of the sintered bodies were observed using FE-SEM (Field Emission Scanning Electronic Microscope; JSM-6700F, JEOL, Japan). EDS micro-region analysis (INCA300, Oxford Instrument, England) was carried out on 4 randomly selected positions in the fracture surfaces of the samples with and without 4 wt.% MgO after washing with 15 vol.% HF solution for 20 min and then drying at 120 °C.

The linear thermal expansion coefficients (LTEC) of the sintered samples were measured in a horizontal dilatometer over the temperature range of 25–1000 °C at a heating rate of 10 °C/min. The sintered discs were characterized using XRD (Cu Kα radiation; D8 ADVANCE, Bruker Corporation, Germany) to determine the final phase assemblage.

3. Results and discussion

3.1. Sintering behaviors with different magnesia contents

3.1.1. Dilatometric measurement

Fig. 1 displays the sintering behavior of the flyash-based mullite with 0–4 wt.% MgO. The sample without MgO exhibits low shrinkages at all temperatures, indicating a poor sintering activity. The sintering process (>900 °C) can be divided into three typical stages: (i) the first shrinkage stage at 977–1318 °C; (ii) the second unique self-expansion stage at 1318–1495 °C; and (iii) the third re-shrinkage stage (1495–1550 °C). These were well discussed in the previous report.[11]

Because of MgO addition (2 wt.% and 4 wt.%), the sintering activity was obviously improved. On the one hand, the addition of MgO resulted in higher shrinkage in the high temperature