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Synthesis and thermo-mechanical properties of mullite–alumina composite derived from sillimanite beach sand: effect of ZrO_2

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Abstract

A mullite–alumina composite was developed by reaction sintering of sillimanite beach sand and calcined alumina. ZrO_2 (2–6 wt.%) was added as additive. The raw materials and additive were mixed, attrition milled and sintered in compacted form at 1400–1600°C with 2 h soaking. The effect of ZrO_2 on the densification behaviour, thermo-mechanical properties and microstructure was studied. It was found that addition of ZrO_2 slightly retards the densification process. All the samples achieved their highest bulk density at 1600°C. Thermo-mechanical properties of the sintered samples are not effectively altered by the presence of ZrO_2. ZrO_2 containing samples always show better resistance to thermal shock than the ZrO_2 free samples. Scanning electron micrography shows that ZrO_2 occupies both an intergranular and intragranular position in the mullite matrix. The mullite formed at 1600°C is mostly equiaxed in nature that suggests densification mainly occurs through solid state sintering.

Keywords: B. Composites; C. Thermal shock; D. Mullite; Flexural strength; Sillimanite sand

1. Introduction

Sillimanite beach sand is a byproduct generated during the extraction of rare earth compounds from beach sand minerals. The estimated reserves of sillimanite beach sand in India are about 54 million tonnes [1]. Attempts have been made by many investigators to utilise this mineral [2–6]. Sillimanite beach sand can be utilised to develop a mullite–alumina composite by reaction sintering with alumina. Mullite–alumina composites have potential application in both shaped and monolithic refractories. Sillimanite sand on heating decomposes to mullite and silica

$$3(Al_2O_3 \cdot SiO_2) = 3Al_2O_3 \cdot 2SiO_2 + SiO_2$$

The released silica reacts with impurities to form a vitreous phase which impairs the product quality. The product quality can be improved by adding excess alumina into the batch to eliminate the possibility of free silica, thereby producing the mullite–alumina composite. Although a number of authors have studied such composites utilising various raw materials, investigations based on sillimanite beach sand are limited [7–11].

The present investigation was undertaken to develop mullite–alumina composites by the reaction sintering of sillimanite sand and calcined alumina. Since the beach sand minerals contain zircon there is the possibility of the presence of minor amounts of ZrO_2 in it. In this investigation the effect of ZrO_2 on the densification, thermo-mechanical properties, thermal shock resistance and microstructure of the composite has been studied. Attempts have been made to characterise the mullite formed and to determine the solid solubility of ZrO_2 within the mullite phase.

2. Experimental

The major raw materials used in this study were beach sand sillimanite and calcined alumina. Beach sand sillimanite was obtained from Indian Rare Earths Limited (IREL), India and calcined alumina from Indian Alu-

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minium Company Ltd. (INDAL), India. Chemical analysis of both the raw materials was done by conventional wet chemical methods. Batch compositions were selected in such a way that they contain 80.75 wt.% Al_2O_3 (in Al_2O_3/SiO_2 ratio); 2–6 wt.% ZrO_2 was added as additive (Table 1).

The batches as per table 1 were attrition milled separately in water medium using a zirconia tank and zirconia grinding media for an optimum time period of 9 h [6]. The resulting slurries were dried at 110 ± 5°C and sieved to break up agglomerates. Rectangular bars having dimension $60\times6\times6$ mm were fabricated by uniaxial pressing at 100 MPa using 5% PVA solution as binder followed by cold isostatic pressing at a pressure of 175 MPa. Green samples were dried at 110 ± 5°C and fired in the temperature range of 1400–1600°C with a 2 h soaking time in an electric furnace. The heating rate was 5°C min^{-1} up to 1100°C and thereafter 3°C $min.^{-1}$ up to the final firing temperature. The sintered products were characterised in terms of bulk density, apparent porosity, flexural strength at room temperature (RT) and at elevated temperatures, thermal shock resistance, phase assembly and microstructure.

The apparent porosity and bulk density of the sintered compacts were measured by the conventional liquid displacement method using Archimedes' principle in water medium.

X-ray powder diffraction patterns of the fired products were obtained in an X-ray diffractometer using nickel filtered Cu-K_α radiation. Diffraction pattern were recorded for the Braggs' angle (2θ) range 15–60°.

Flexural strength was determined by standard three point bending method in an instrument (INSTRON) with a span length of 40 mm and cross head speed of 0.5 mm/min using sintered bars having dimension $55\times5\times5$ mm. The samples used were polished and the edges were chamfered with a diamond disc. The hot MOR was determined by the same method after a dwell period of 30 min.

Thermal shock resistance of the samples was studied by measuring the retained flexural strength after multiple air quenching cycles from 1000°C to ambient air. For this purpose the samples were heated to 1000°C in an electric furnace with a soaking period of 30 min, then quenched in ambient air, kept for 10 min followed by sudden reheating at 1000°C for 10 min. This cycle was repeated and the retained flexural strength was measured at a regular interval of 2 cycles. Three samples were taken to determine the retained flexural strength at each test and the average values have been reported here.

Microstructure evaluation and elemental analysis of the mullite grain of the sintered compacts were done by scanning electron microscopy (SEM) with energy dispersive x-ray (EDX) analysis using a sputtered carbon coating on the polished surface of the sintered samples after thermal etching.

Table 1
Batch composition selected and sample codes used for the study

Sample code	Sillimanite sand (wt.%)	Calcined alumina (wt.%)	ZrO_2 content (wt.%)
C	48.29	51.71	–
CZ2	47.32	50.68	2.00
CZ4	46.35	49.65	4.00
CZ6	45.39	48.61	6.00

3. Results and discussion

3.1. Raw materials characterisation

Chemical analyses of the raw materials are given in Table 2. The silica content of the sillimanite sand is higher than the stoichiometric amount, and this excess silica present as quartz [3]. The alumina used in this investigation was calcined alumina consisting of only α-Al_2O_3. The average particle size of the sillimanite powder was 4.5 μm and calcined alumina was 5.0 μm.

3.2. Densification

The bulk density of the sintered samples is a measure of both chemical reaction and densification. Variations of the bulk density of the mullite-alumina composites with sintering temperature are shown in Fig. 1. In all cases the bulk density increases with increase in sintering temperature; the highest bulk density is reached with an apparent porosity of $<0.5\%$ at 1600°C. It was found that at 1600°C the bulk density was dependent on the ZrO_2 content. It increases from 3.28 g/cc for C to 3.39 g/cc for CZ6. Higher specific gravity of the ZrO_2 is responsible for this. In the absence of any additive, the densification of C sample occurs mostly through solid state sintering with small amounts of glass formation due to the presence of impurities in the raw materials [3]. ZrO_2 addition slightly retards the densification by reducing the glassy phase at the sintering temperature.

Table 2
Chemical analyses of raw materials

Constituents (wt.%)	Sillimanite sand	Calcined alumina
Al_2O_3	57.60	99.30
SiO_2	40.30	–
Fe_2O_3	0.31	–
TiO_2	0.11	–
CaO	0.42	–
MgO	0.31	–
Na_2O	–	0.30
K_2O	0.02	–
LOI	0.70	–

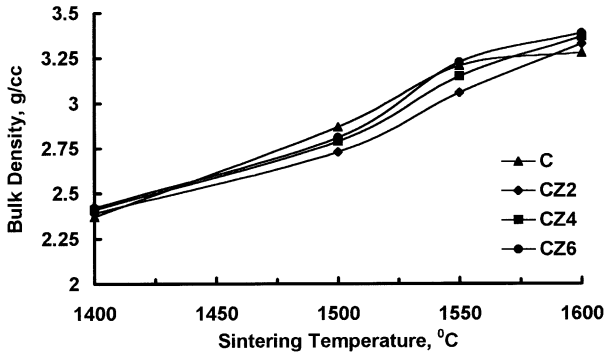

Fig. 1. Variation of bulk density of the samples containing ZrO_2 with the sintering temperature.

3.3. Microstructure

X-ray diffraction pattern of the sample CZ4 sintered at 1600°C is shown in Fig. 2. It was found that, the major crystalline phase was mullite with some amount of corundum. A small amount of zirconia both in monoclinic and tetragonal form was also noticed. Scanning electron photomicrographs of the samples C and CZ6 sintered at 1600°C are shown in Fig. 3(a) and (b). Since the densification mostly occurs through solid state sintering, the mullite grains formed are mostly equiaxed in nature [7]. From Fig. 3(a) and (b) it was found that the presence of ZrO_2 slightly reduces the mullite grain growth and amount of glassy phase [12]. ZrO_2 particles mostly occupy the intergranular position within the mullite matrix. Small amounts of finer ZrO_2 particles are also noticed in the intragranular position. EDX spectra of a mullite grain of the sample CZ6 sintered at 1600°C is shown in Fig. 4. From this figure it is seen that, ZrO_2 enters in the mullite structure by solid solution formation. Elemental analysis shows that the Al_2O_3/SiO_2 molar ratio of mullite formed in sample CZ6 is 2.0777 indicating the nonstoichiometric nature of the mullite, and 1.70 wt.% ZrO_2 enters in the mullite structure by solid solution formation.

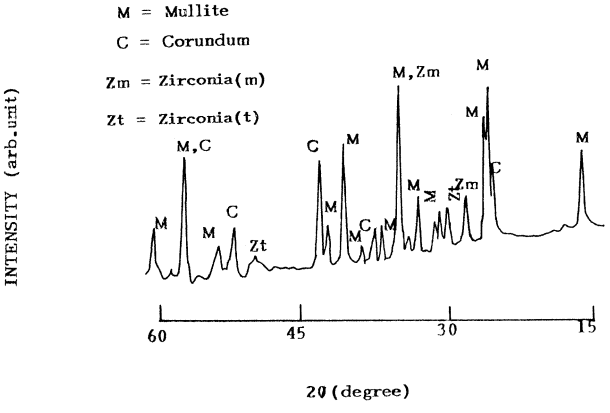

Fig. 2. XRD pattern of the samples CZ4 sintered at 1600°C.

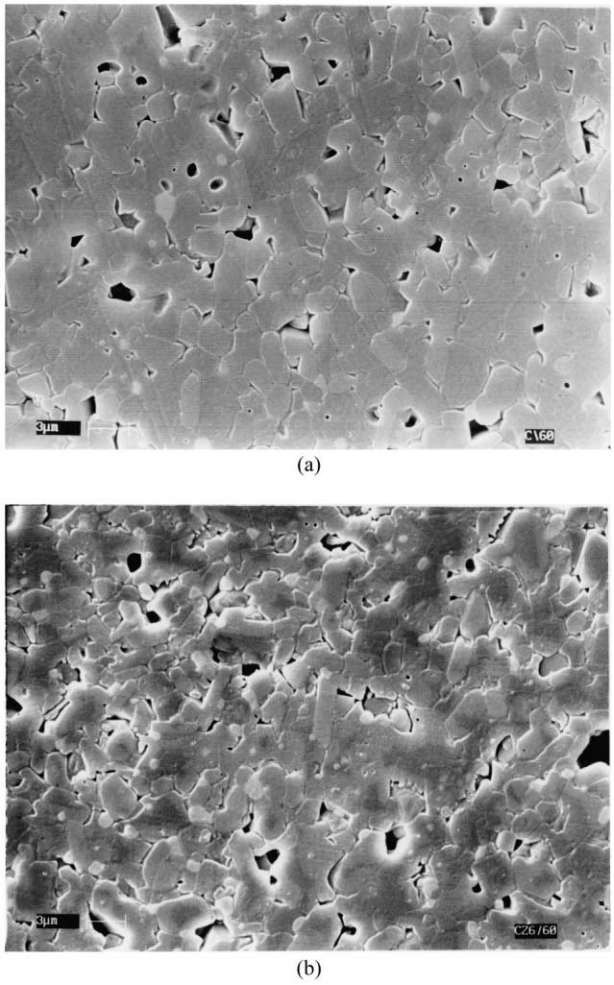

Fig. 3. Scanning electron photomicrograph of the samples sintered at 1600°C: (a) sample C (b); sample CZ6.

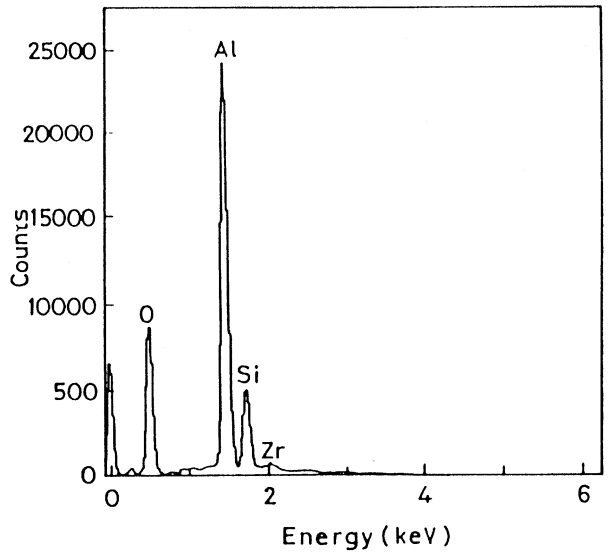

Fig. 4. EDX spectra of the mullite grain of the sample CZ6 sintered at 1600°C showing the solid solution of ZrO_2 within the mullite.

3.4. Strength

Flexural strength at room temperature is determined by the distribution of the residual glassy phase, whereas flexural strength at higher temperature depends on the nature of the residual glassy phase which softens during testing [13]. Variation of hot MOR at 1200°C with ZrO_2 content and sintering temperature is shown in Fig. 5. ZrO_2 containing samples sintered at 1400–1550°C show slightly lower hot MOR than ZrO_2 free samples due to its lower bulk density (Fig. 1) and higher amount of porosity. Since all the samples achieve almost zero porosity (<0.5%) on firing at 1600°C, ZrO_2 addition increases the flexural strength of the samples when sintered at 1600°C. Hot MOR increases from 235.4 MPa for sample C to 278 MPa for sample CZ6.

Samples sintered at 1600^{0}C were used to measure the flexural strength at different temperatures and the results are depicted in Fig. 6. All the samples show the usual behaviour of high alumina materials with a small amount of high silica vitreous phase. From Fig. 6 it is seen that there is a slight decrease in strength with increase in temperature up to 600–900°C followed by an increase in strength up to 1200°C. The initial decrease in strength is related to the elastic bond relaxation with increase in temperature, and the final strength enhancement at higher temperature (above ~900°C) is due to the softening of residual glassy phase at the test temperature range which could lead to the healing of critical flaws or increase in apparent toughness [13–15].

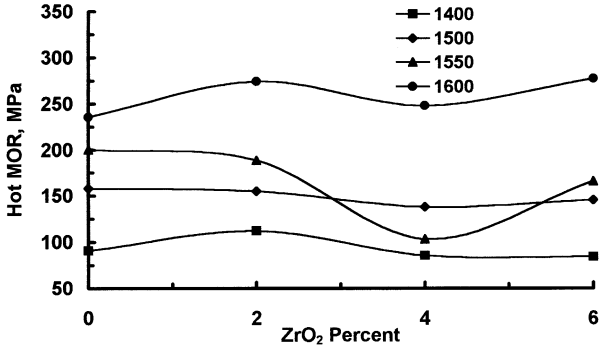

Fig. 5. Variation of hot MOR at 1200°C with sintering temperature and ZrO_2 content.

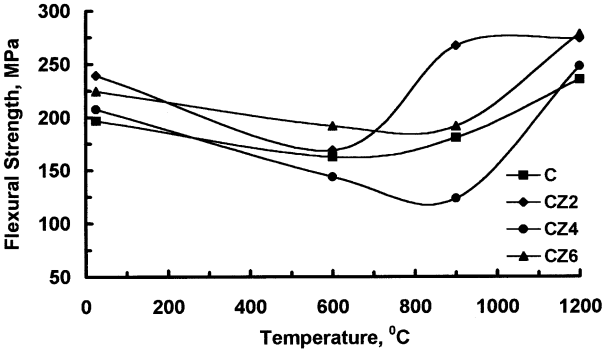

Fig. 6. Variation of flexural strength of the samples sintered at 1600°C with the temperature.

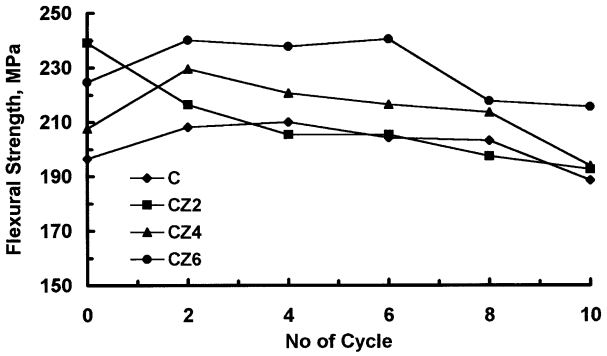

Fig. 7. Variation of retained flexural strength of the samples sintered at 1600°C with the number of cycles.

3.5. Thermal shock resistance

Samples sintered at 1600°C were used to study the thermal shock behaviour. Retained flexural strength of the samples with regard to multiple thermal shock quench cycles from 1000°C to room temperature are shown in Fig. 7. It can be seen that in all the cases there is strength enhancement up to 2nd cycle and in most of the cases strength degradation starts after 6th cycle. Similar phenomenon was noticed with Fe_2O_3 addition in an earlier investigation [16]. The initial strengthening is due to the effect of tempering [16–18]. Strength degradation after 6th cycle is due to the thermal fatigue by subcritical crack growth. Presence of ZrO_2 improves the thermal shock resistance of the samples, may be due to the reduction of amount of glassy phases in the sintered samples.

4. Conclusion

Sillimanite beach sand can be used to develop mullite-alumina composite by reaction sintering with alumina. ZrO_2 addition into the batch does not effectively alter the densification process or thermo mechanical properties of the composite. ZrO_2 containing samples always show higher thermal shock resistance than the ZrO_2 free samples. All the samples exhibit a strength enhancement after thermal shock up to 2nd cycles. Mullite grains are equiaxed in nature. ZrO_2 mostly remains in the intergranular position within the mullite matrix and reduces the grain growth. Mullite formed is nonstoichiometric in nature and maximum solid solubility of ZrO_2 within the mullite structure is 1.70 wt.%

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