

Synthesis of mullite aggregates from fly ash: effect on thermomechanical behaviour of low cement castables

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Refractory aggregates were synthesised from beneficiated fly ash by reaction sintering with calcined alumina at 1600°C, and 83% mullite yield was achieved. The aggregates had low porosity, low thermal expansion and good refractoriness. To study compatibility in castable refractories, the aggregates were used in high alumina cement based low cement castables and their thermomechanical behaviour was studied. Microstructural characterisation revealed that the emergence of new bond phases such as mullite and calcium hexa-aluminate had a beneficial effect on the hot modulus of rupture and creep resistance of castables. An attempt was made to establish a structure-property relationship. BCT/0402

Keywords: Fly ash, Low cement castable, Mullite, Synthesis, Thermomechanical properties.

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INTRODUCTION

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only aluminosilicate phase in the Al_2O_3 - SiO_2 binary system that has high temperature stability at atmospheric pressure. It is a desirable phase for high temperature applications owing to its low thermal expansion, good thermal shock resistance, high creep resistance and strength retention at elevated temperature.¹⁻⁴ Owing to its excellent thermomechanical properties, mullite is considered an ideal candidate material for castable applications.⁵ A number of natural and synthetic minerals have been used to synthesise mullite for refractory applications. Pure Al_2O_3 - SiO_2 powder,⁶ kaolin,⁷ kyanite⁸ and sillimanite⁹ all have the potential to produce mullite on thermal treatment.

Fly ash is a byproduct of thermal power plants resulting from combustion of pulverised coal. The major constituents of fly ash are SiO_2 and Al_2O_3 and it is thus often used in ceramic industries as a low cost source of aluminosilicates.¹⁰ Interest in the use of fly ash for the synthesis of mullite developed in the early 1990s. Ohtake *et al.*¹¹

prepared mullite from a 1:1 mixture of pretreated fly ash and α - Al_2O_3 and achieved 80% mullite yield at 1673 K. It is reported that mullite synthesised from beneficiated fly ash gives comparable mechanical and thermal properties to industrial mullite.¹² Huang *et al.*¹³ reported that mullite synthesised from class F fly ash has better mechanical properties than that synthesised from class C fly ash. Mitra *et al.*¹⁴ studied the refractory properties of mullite prepared from a mixture of fly ash and bauxite and found that it could withstand seven cycles of thermal spalling. Kumar¹⁵ synthesised mullite aggregate from a mixture of beneficiated fly ash and calcined alumina for castable applications and studied hydraulic and thermal properties in relation to pure calcium aluminate phases. Aggregates with pure calcium aluminate phases such as CA, CA2 and C12A7 and their various combinations were used, and excellent strength was obtained after various hydration times as well as good hot modulus of rupture in the temperature range 1000-1250°C. Das *et al.*¹⁶ used similar fly ash derived aggregate in regular castables and found it suitable for moderate temperature application.

In the present work, beneficiated fly ash and calcined alumina were used to synthesise mullite aggregates. To study the suitability of these aggregates in low cement castables (LCCs), an LCC model was designed using the aggregates and commercial high alumina cement. The focus of the study is on thermomechanical behaviour of this LCC. The overall aim of the study is to reduce the cost of mullite production by using inexpensive material and fly ash for high added value structural products, and also to limit environmental problems associated with the disposal of fly ash.

EXPERIMENTAL PROCEDURES

Synthesis and characterisation of aggregates

The starting materials were fly ash and calcined alumina collected from Nalco, India. The fly ash was mixed with water and passed through a high power magnetic separator (Eriez wet high intensity magnetic separator) to remove the iron bearing particles. Chemical analyses of the beneficiated fly ash and calcined alumina are given in Table 1. The main impurity was Fe_2O_3 : a content of 4.66% in raw fly ash was reduced to 1.9% by magnetic separation.

The beneficiated fly ash was wet milled along with calcined alumina and kaolinite in a pot mill for 8 h, screened to remove coarser particles, dried at 110°C, powdered to break up the agglomerate and compacted using uniaxial pressing at 80 MPa. Sintering was carried out in an electric furnace at 1600°C for 2 h in an oxidising atmosphere. The heating rate was kept at 5 K min⁻¹ with 1 h soaking time at 1300°C. Sintered samples were slowly cooled to room temperature, then crushed and graded into different aggregate sizes.

Chemical analysis of raw materials as well as of sintered aggregates was carried out by a conventional wet chemical method. The phases formed after sintering were identified

using a Siemens D500 X-ray diffractometer with Ni filter and Cu K_{α} radiation. A scanning electron microscope with EDX probe (Jeol JSM 840A) was used to examine microstructure. The bulk density (BD) and apparent porosity (AP) of the sintered specimens were determined by a water displacement method using Archimedes' principle. Coefficients of thermal expansion were determined using a dilatometer (Netzsch) in the range 50–900°C. Pyrometric cone equivalent (PCE) values were obtained by heating the samples and comparing with Orton cones in a PCE furnace.

Preparation and characterisation of LCC

An Andreassen distribution pattern¹⁷ with a q value of 0.26 was used to design the LCC model. Commercial high alumina cement (75%Al₂O₃) was used as a hydraulic binder. The design of the LCC is given in Table 2. The raw materials were dry mixed for 5 min and then mixed for a further 5 min with water. The flow value was measured using a truncated flow cone according to the ASTM C230 standard. The castable mix was cast into 50 × 50 × 50 mm cubic briquettes for measurement of BD, AP and cold crushing strength (CCS) by vibration casting. The samples were cured for 24 h in a humidity chamber (≈95% RH) and then heat treated at 110, 200, 400, 600, 800, 1000, 1200, 1400, 1500°C for 2 h in air. Cold crushing strength was measured using an Ansler (Germany) universal testing machine. Bulk density and apparent porosity of castables were measured after heating at each test temperature.

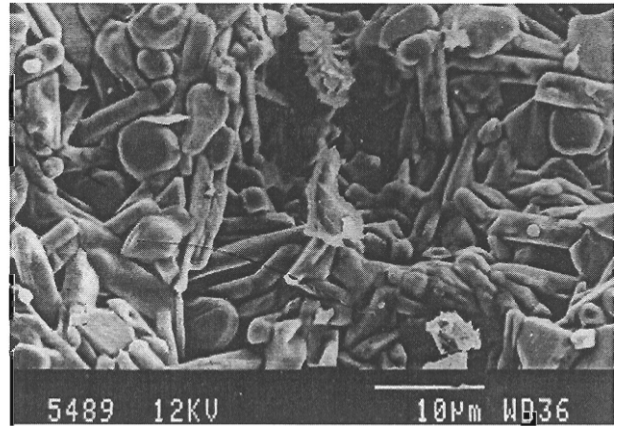
Hot modulus of rupture (MOR) was measured on 150 × 25 × 25 mm bars in three point bending at various temperatures using a Netzsch high temperature bending strength tester. An average of six samples was used for each test. Modulus of rupture of LCC samples was determined at 1200, 1300, 1400 and 1500°C. Creep of prefired castable samples was tested on 50 mm diameter cylindrical samples with 50 mm height using a Netzsch creep testing machine at 1250 and 1400°C. Creep testing of unfired samples was avoided, since there is the possibility of crumbling of samples in compression. Samples were heated for 25 h and their deformation against time was recorded. XRD and SEM were carried out on LCC samples heat treated at 1400 and 1500°C using the same instrument and parameters as mentioned above.

RESULTS AND DISCUSSION

Characterisation of aggregates

The chemical analyses and physical properties of the synthetic aggregates are given in Tables 3 and 4. The aggregates are close to mullite in composition. More than 91% of the theoretical density of mullite was achieved. The low apparent porosity (0.95%) is due to a dense network of crystals. The pyrometric cone equivalent value of 38 demonstrates suitability for high temperature application. The coefficient of thermal expansion of 5.4×10^{-6} is close to that of commercial mullite.

XRD of the aggregates revealed that the major phase was mullite, with a minor corundum phase. Both spherical and elongated grains of mullite were observed (Fig. 1), but the majority were elongated, indicating the presence of an intergranular glassy phase, as also reported by Dekeyser.¹⁸



1 Scanning electron micrograph of synthesised mullite aggregates

Characterisation of LCC

Cold crushing strength, bulk density and apparent porosity

Variation of the cold crushing strength, apparent porosity and bulk density of low cement castable briquettes with heating temperature is shown in Fig. 2. The variation in all three properties up to 1000°C is due to the high alumina cement. The improved strength at 110°C is due to increased crystallinity of different gels formed by hydration of

Table 2 Design of low cement castable (wt-%)

Mullite aggregates	
–74 μm	20
0–0.4 mm	22
0.5–3 mm	30
2–4 mm	10
High alumina cement	6
Microsilica	6
Reactive alumina	6
Dispersant	0.2
Water to cast	6
Vibration induced flow, mm	134

Table 3 Chemical analysis of synthesised mullite aggregate (wt-%)

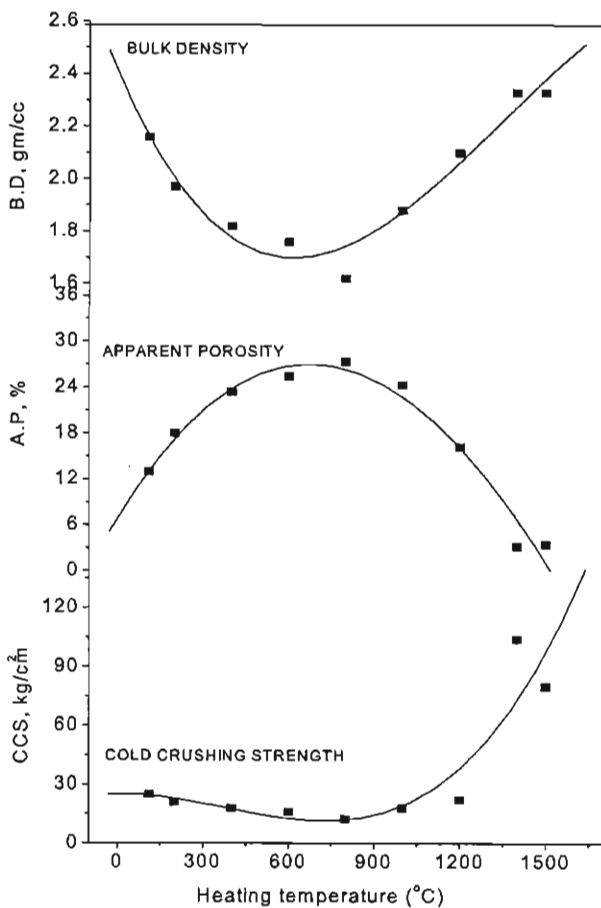
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O
26.31	71.18	0.66	0.32	Trace	0.22	...

Table 4 Physical properties of synthesised mullite aggregate

Colour	Very light brown
Bulk density, g cm ⁻³	2.89
Apparent porosity, %	0.95
PCE (Orton cones)	38
Thermal expansion coefficient	5.4×10^{-6}
Compressive strength, MPa	980
Change on reheating (1600°C), %	0
Phases present	Mullite, corundum

Table 1 Chemical analysis and physical properties of beneficiated fly ash and calcined alumina

Material	Chemical analysis, wt-%								LOI	Colour	Bulk density, g cm ⁻³	Surface area, cm ² g ⁻¹
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	...				
Fly ash	62.95	28.78	1.90	1.73	0.33	0.92	...	2.18	Grey	2.01	3960	
Calcined alumina	0.03	99.50	0.02	0.05	0.3	0.2	White			

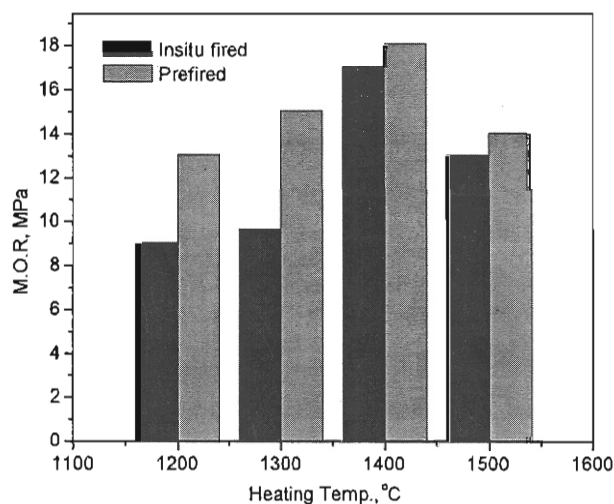


2 Variation in cold crushing strength, apparent porosity and bulk density of LCC with heating temperature

calcium aluminates. Strength loss in the region 200–1000°C is due to breaking of hydraulic bonds and is a well known phenomenon in refractory castables. The increase in strength above 1000°C indicates the beginning of ceramic bond formation. The maximum strength in the samples fired at 1400°C may be related to the formation of a dense network of mullite crystals, which strengthens the structure at high temperature.¹⁹ This observation is further supported by bulk density results, where maximum density was found in the castables fired at 1400°C. The increase in porosity and decrease in bulk density in the temperature range 200–1000°C is due to evaporation of water causing porous castable body structure. The increase in density and decrease in porosity above 1200°C shows the beginning of densification and liquid phase formation, which occupies the pore spaces. The minimum porosity in the samples fired above 1400°C can be explained by the formation of a viscous phase which fills the spaces between the constituents of the castables.

Hot modulus of rupture

Figure 3 shows the modulus of rupture values of *in situ* and prefired LCC as a function of temperature. The low MOR at 1200 and 1300°C in the case of *in situ* fired samples indicates the initial sintering stage where densification and phase formation has just started. An improved MOR at 1400°C is related to the precipitation of mullite from the melt containing silica and alumina. A similar mechanism of mullite precipitation in tabular alumina based refractory castables has been reported.²⁰ Extensive formation of a liquid phase at 1500°C reduced the MOR values. In prefired samples, the MOR increased with temperature, reached a maximum at 1400°C and then decreased. This trend may be

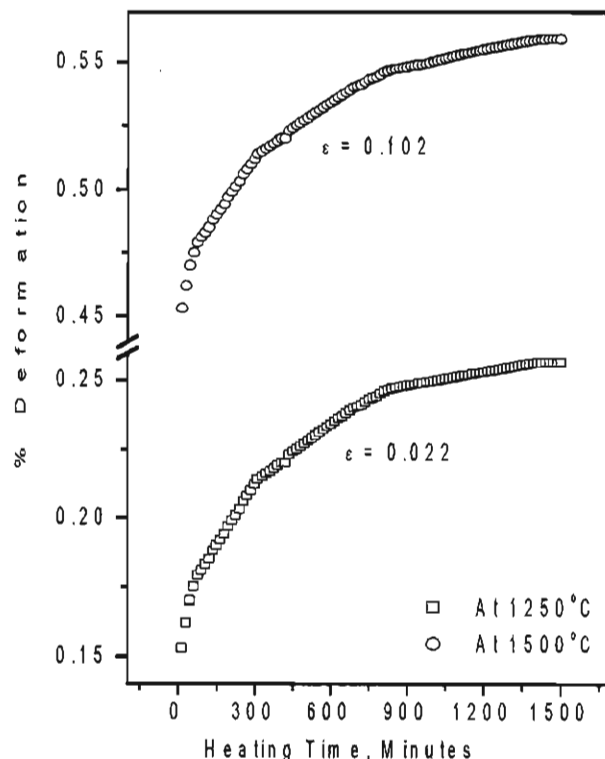


3 Hot modulus of rupture of LCC at different temperatures

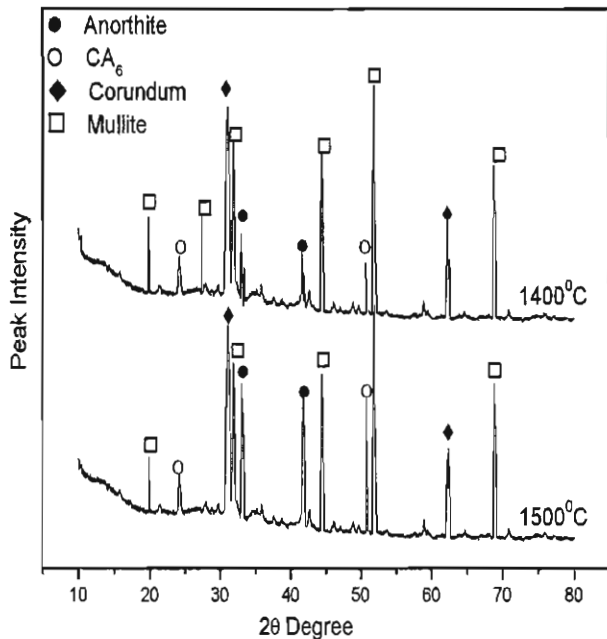
due to the mineral phases, which had already formed during prefiring. Aggregate strength, compatibility between different aggregates and compatibility between aggregates and the bond phase with respect to thermal expansion coefficient further influenced the hot MOR values in all cases.

Creep

The creep test is one of the most important tools for refractory matrix engineering. Creep rate is a very sensitive indicator of changes in glass phase composition, grain size and microstructure.²¹ Figure 4 shows the creep deformation curve of low cement castable at 1400 and 1500°C. At both temperatures, deformation started after reaching the test temperature and increased with heating time. The rate of deformation stabilised after 15 h of heating at 1400°C and deformation between 5 to 25 h was found to be 0.002%. This low deformation is a result of the formation of fine



4 Creep deformation curve of LCC at different temperatures



5 XRD of LCC heat treated at 1400 and 1500°C

needles of mullite as an interaggregate compound. At 1500°C on the other hand, deformation continues for 20 h at a rate of 0.023% per hour. Formation of a more viscous phase in the interaggregate zone, where coarse aggregates are considered to be rigid, leads to a grain boundary displacement mechanism and a high deformation rate.²² In order to understand the deformation mechanism, SEM of creep tested samples was carried out and the results are discussed below.

Microstructural studies

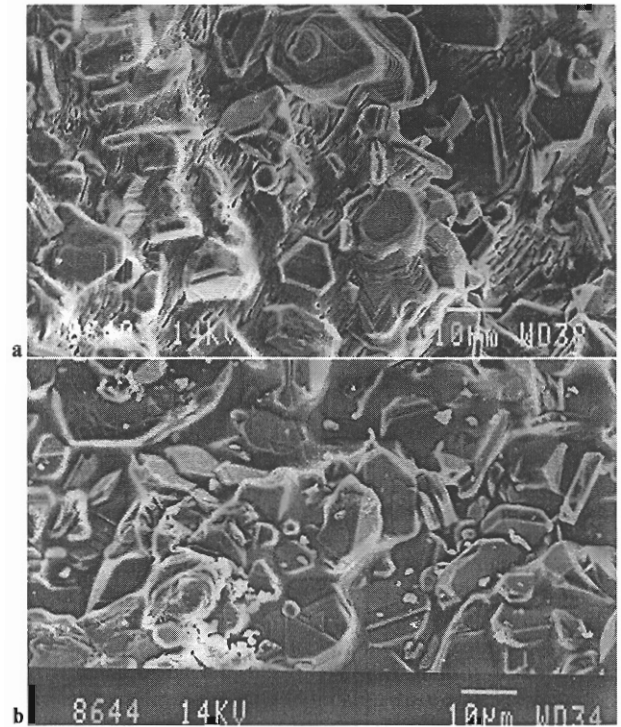
The XRD patterns of castable samples heat treated at 1400 and 1500°C are shown in Fig. 5. In the LCC fired at 1400°C, the major phases identified were mullite (JCPDS 15-776), corundum (10-173), anorthite (12-301, 20-20) and calcium hexa-aluminate (38-470). The peak intensity of anorthite and calcium hexa-aluminate was more pronounced in the samples fired at 1500°C.

Figure 6 shows SEM micrographs of LCC fired at 1400 and 1500°C. In the 1400°C fired samples (Fig. 6a), fine needle shaped crystals occupy the space between larger grains. EDX analysis confirmed that these needle shaped crystals have a composition close to mullite. The fine mullite needles give reinforcement to larger grains, leading to a strong structure and consequently to good hot MOR and creep resistance at 1400°C. Most of the pores are concentrated in the matrix of mullite needles at the trijunctions of bigger grains. In 1500°C fired samples (Fig. 6b), the interaggregate space is filled by a glassy phase. These viscous phases might have promoted grain boundary sliding motion, causing loss of hot MOR and creep resistance.

Micrographs of creep tested LCC samples are shown in Fig. 7. A compact microstructure was observed in samples tested for creep at 1400°C (Fig. 7a). In the case of LCC tested for creep at 1500°C (Fig. 7b), a deformed microstructure dominated by exaggerated grain growth and glassy phase was observed, indicating high deformation rate and inferior properties.

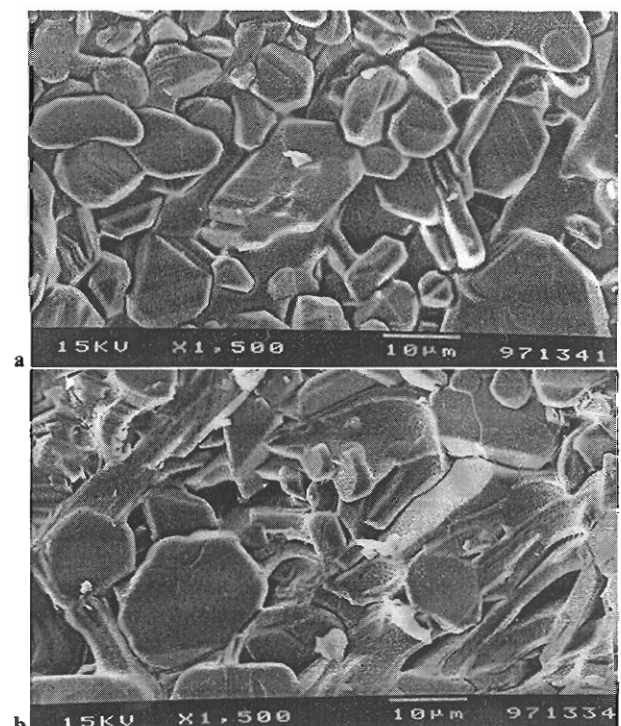
CONCLUSIONS

Mullite aggregates synthesised from a fly ash and alumina mix consisted of a dense crystal network of mullite and corundum. The aggregates had good hot modulus of



6 Scanning electron micrographs of LCC heat treated at a 1400 and b 1500°C

rupture, thermal expansion coefficient and refractoriness. Improved compressive strength of LCC above 1200°C resulted from the formation of new phases that occupied the pore space and gave reinforcement to the structure. The good hot MOR at 1400°C was a combined function of aggregate strength, mullite formation in bonding phase and compatibility of aggregate with aggregate and aggregate with bond phase. Formation of mullite needles as an interaggregate compound improved creep resistance.



7 Scanning electron micrographs of LCC tested for creep resistance at a 1400 and b 1500°C

Above 1400°C, loss of hot MOR and creep resistance was due to greater liquid phase formation. The aggregate synthesised from fly ash can be safely used in castables up to a temperature of 1400°C.

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