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Thermo-mechanical behaviour of low cement castables derived from mullite aggregates synthesised from beach sand sillimanite

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Abstract

Mullite aggregates were synthesised from beach sand sillimanite, a by-product generated during rare earth extraction, by reaction sintering with calcined alumina. The aggregates were characterised in terms of chemical composition, mineral phases, microstructure and important thermo-mechanical properties critical for refractory applications. To evaluate its suitability in castable refractories, low cement castables were prepared using the aggregates with commercial high alumina cement. The physical and thermo-mechanical properties such as bulk density, apparent porosity, cold crushing strength, hot modulus of rupture and compressive creep was studied in relation to temperature. The castables exhibited good modulus of rupture and excellent creep resistance at 1400 °C. Attempts were made to correlate these properties with corresponding microstructure and phases.

Keywords: D. Mullite; Beach sand sillimanite; Synthesis; Low cement castables

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1. Introduction

With the depleting natural resources of high-grade alumina bearing raw material for refractory industries in India, there is a need to find out alternate sources. One of such source may be Beach sand sillimanite (BSS) deposit, which generated during the extraction of rare earth compounds. The BSS reserves in India are estimated to be around 54 million tonnes, out of which a very small percentage are being used in refractory industries and rest remains unused as waste. The Indian BSS contains about 50–60% Al_2O_3 and thus can be considered as low cost alumina raw material. However, the study on BSS is limited due to its occurrence in only few countries.

Thermal transformation of sillimanite is widely investigated by many workers [1–3]. Sillimanite breaks into mullite and silica on heating under oxidising condition according to following reaction [2]:

$$3Al_2SiO_5 \rightarrow 3Al_2O_3{\cdot}2SiO_2 + SiO_2$$

To achieve the high mullite yield, additional alumina is introduced into the system, which reacts with the remaining silica and forms mullite. Use of BSS for the synthesis of mullite was reported by Tripathy et al. [4,5]. They studied the effect of different additives such as TiO_2 and ZrO_2 on the sintering characteristic and thermo-mechanical behaviour of mullite derived from BSS. Literature is also available on use of such BSS derived mullite for castable applications. Kumar [6] developed the refractory aggregate from BSS with the composition close to mullite and studied their hydration and thermal properties in relation to pure calcium aluminate phases. He obtained good HMOR values at 1400 °C when used with different combinations of CA, CA_2 and $C_{12}A_7$ cement. The same aggregate was used with commercial high alumina cement in regular castables and its hydraulic and high temperature properties were investigated by Das et al. [7]. They reported a good crushing strength value when fired above 1200 °C.

On the basis of available literatures, it is found that BSS derived mullite aggregate shows compatibility in high alumina cement based regular castable. Need is felt to study the suitability of these aggregates for low

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cement castables, which is the object of present investigation. Low cement castable (LCC) model was designed using the aggregates and commercial high alumina cement. A systematic study was carried out on the physical and thermo-mechanical properties of LCC as a function of temperature. Attempts were made to correlate the properties with corresponding phases and microstructure.

2. Experimental

2.1. Synthesis and characterisation of aggregate

Beach sand sillimanite from Indian Rare Earths Ltd., India (SiO_2—35.11, Al_2O_3—60.27, Fe_2O_3—0.56, CaO—1.25, TiO_2—0.68, L.O.I—0.88 wt%) and calcined alumina from NALCO, India (Al_2O_3—99.5, Na_2O—0.3, CaO—0.05, Fe_2O_3—0.02, SiO_2—0.03, L.O.I—0.2 wt.%, α-content >95%) were used as starting material for the synthesis of mullite. The raw materials along with additives were wet milled for 12 h, screened to remove coarser particles, dried at 110 °C, powdered to break the agglomerate and compacted by uniaxial pressing of 80 MPa. The shaped samples were fired in an electric oven at 1600 °C for 2 h in oxidising atmosphere. The rate of heating was kept 5 °C/minute with 1 h soaking at 1300 °C. Sintered samples were slowly cooled to room temperature, then crushed and graded into different aggregate size. The chemical analyses of raw materials and sintered aggregates were carried out by conventional wet chemical analysis methods. The phases formed after sintering were identified by XRD (Siemens D 500) using Ni filter and Cu(K_α) radiation. Jeol JSM 840 A scanning electron microscope with EDX probe was used to examine the microstructure. The bulk density (BD) and apparent porosity (AP) of the sintered specimens were determined by the water displacement method using Archimedes Principle. The coefficient of thermal expansion (CTE) was determined using a Dilatometer (NETZSCH) in the range of 50–900 °C. Heating the samples in comparison with Orton cones gave the Pyrometric cone equivalent (PCE) values.

2.2. Preparation and characterisation of low cement castable

Commercial high alumina cement (Cal Al 75, Source ACC, India) was used as hydraulic binder for castable preparation. The castable model was designed on Andreassen distribution pattern [8] with q value = 0.22. The composition of low cement castable is given in Table 1. The raw materials were dry mixed for 5 min, and then mixed for 5 min with water. The flow value was measured using truncated flow cone according to ASTM C230 standard. The castable mix was cast into 50×50×50 mm cubic briquettes for BD, AP and cold crushing strength (CCS) as well as into 150×25×25 mm bars for HMOR and into 50 mm diameter cylindrical samples with 50 mm height for creep studies by vibration casting. The samples were cured for 24 h in curing chamber (>90% RH) and then heat treated at 110, 200, 400, 600, 800, 1000, 1200, 1400, 1550 °C for 2 h in air. The CCS of castable briquettes was measured with an Amsler Universal Testing Machine. The bulk density and apparent porosity of castables were measured after heating at each test temperature.

Table 1
Low cement castable composition

Weight%	LCC
Mullite aggregates	
−74 micron	20
0–0.4 mm	22
0.5–3 mm	30
2–4 mm	10
Calcium aluminate cement	6
Microsilica	6
Reactive alumina	6
Dispercent	0.2
Water to cast	6
Vibration induced flow in mm	138

A high temperature bending strength tester (NETZSCH), equipped with a preheating chamber allowing upto 9 bars to be loaded simultaneously, was used to determine hot modulus of rupture (HMOR) at different temperatures by three-point bending method. An average of six samples was used for each test. The modulus of rupture of LCC samples was determined at 1200, 1300, 1400 and 1500 °C. The measurements were carried out on three type of samples (1) green samples first time heated in situ, (2) sample prefired at test temperature and then cooled to room temperature, and (3) samples prefired for three times (multifired) at test temperature followed by subsequent cooling at room temperature. The compressive creep of the pre-fired LCC samples were tested using a NETZSCH Creep testing machine at 1400 and 1500 °C. The creep study of unfired samples was avoided, as there is a possibility of crumbling the samples under compressive load. Fifty millimetre diameter cylindrical samples were heated for 25 h and the deformation against time was recorded. The XRD and SEM were carried out on the LCC samples heat-treated at 1400 and 1500 °C using the same instrument and parameters as mentioned earlier.

3. Results and discussion

3.1. Characterisation of aggregates

Fig. 1 shows the XRD of the synthesised mullite aggregates. The major phase formed after the sintering

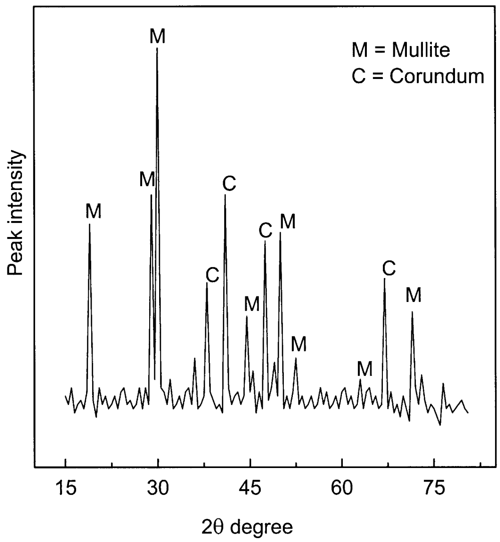


Fig. 1. XRD of mullite aggregate synthesise from BSS.

Table 2
Properties of mullite aggregate synthesised from BSS

Properties	Mullite aggregate
Chemical	
SiO_2	26.52
Al_2O_3	72.65
Fe_2O_3	0.42
CaO	0.52
MgO	–
TiO_2	0.22
Na_2O	–
Physical	
Colour	White
Bulk density (gm/cc)	3.12
Apparent porosity (%)	0.40
Pyrometric cone equivalent	38
Thermal expansion coefficient ($\times10^{-6}$)	5.2
Compressive strength (MPa)	786
Change on re-heating (1600 °C)	0

was mullite. A few corundum peaks were also identified, which may be due to excess of alumina. Presence of controlled amount of impurities like Fe_2O_3 and TiO_2 promoted the reaction sintering at lower temperatures. Tripathy et al. [4] also reported that addition of TiO_2 lowers downs the sintering temperature of BSS. The microstructure of synthesised aggregate examined through SEM is shown in Fig. 2. The majority of the mullite is equiaxed in shape. It seems that each monocrystal of sillimanite converted to mullite in composition but retained the equiaxed shape of original sillimanite grains. The elongated mullite grains are due to presence of inter-granular glassy phase, as also reported by Dekeysen [9]. EDAX analysis revealed that a few spherical grains have compositions close to corundum.

The chemical analysis and physical properties of the synthetic aggregates is shown in Table 2. The aggregates are close to mullite composition. More than 98% of theoretical density to that of mullite was achieved. The low apparent porosity (0.40%) is due to dense network of coarse and fine crystals. The PCE value of 38 shows its suitability for high temperature application. The CTE value 5.2×10^{-6} is close to commercial mullite.

3.2. Characterization of low cement castables

Variation in cold crushing strength of low cement castable in relation to heating temperature is shown in Fig. 3. A good strength was attained at 110 °C as a result of increased crystallinity of high alumina cement. The strength loss in the region of 200–1000 °C is a well known phenomena of refractory castables, which is due to the breaking of hydraulic bond. Gradual increase in strength above 1000 °C indicates the beginning of ceramic bond formation. The maximum strength was achieved at 1500 °C.

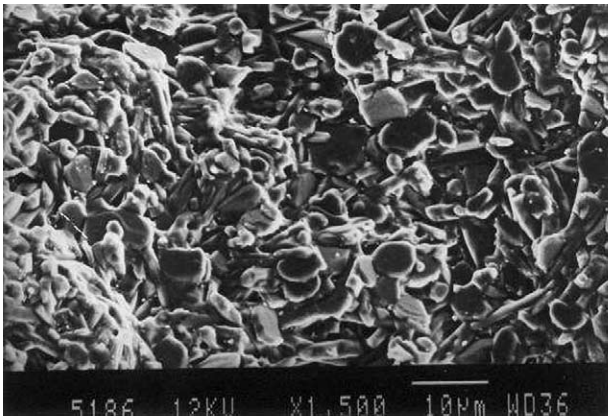


Fig. 2. SEM of mullite aggregate synthesise from BSS.

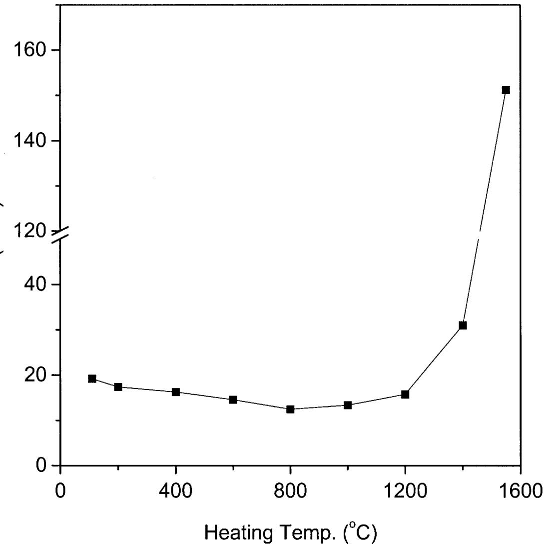


Fig. 3. Variation in CCS of LCC in relation to heating temperature.

Fig. 4 includes the variation in AP and BD in relation to heating temperature. The increase in AP and decrease in BD in the temperature region of 200–1000 °C is due to evaporation of water causing porous castable body structure. Increase in BD and decrease in AP above 1200 °C shows the beginning of densification and liquid phase formation, which occupied the pore spaces. A similar trend of porosity was observed in low cement castables elsewhere [10].

Variation in modulus of rupture as a function of temperature is graphically represented in Fig. 5. In case of in situ heated samples, a good HMOR value was obtained at 1200 °C. The liquid phase formation at 1300 °C caused by the lime present in cement resulted into loss of HMOR. The improvement in HMOR at 1400 °C is due to precipitation of mullite from the melt containing silica and alumina. Myhre [11] reported the similar mechanism HMOR development due to mullite precipitation in tabular alumina based refractory castables. At 1500 °C, formation of more liquid phase reduced the HMOR. A different trend of HMOR development was obtained for prefired and three times fired sample, where the HMOR decreased with temperature. This trend may be attributed to the properties of mineral phases, which already formed during prefiring. Aggregate strength, compatibility between different aggregates and compatibility between aggregates and bond phase in CTE further influenced the HMOR values in all the cases.

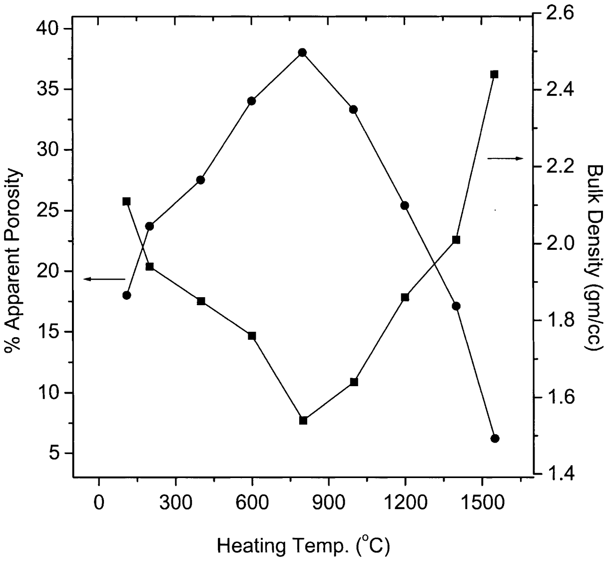


Fig. 4. Variation in AP and BD of LCC in relation to heating temperature.

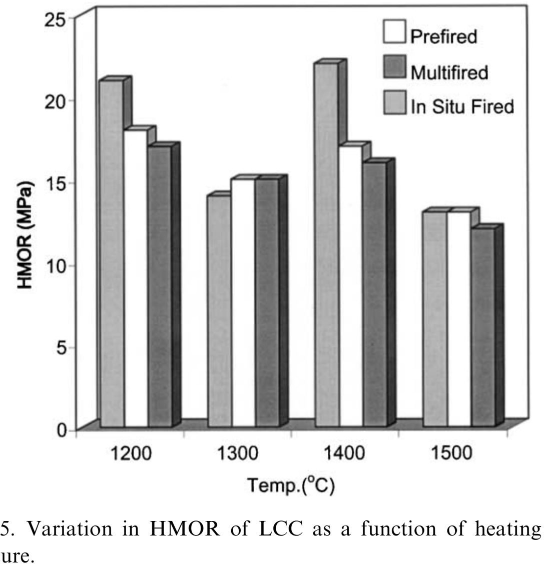


Fig. 5. Variation in HMOR of LCC as a function of heating temperature.

The creep test is one of the most important tools for refractory matrix engineering. The creep rate is a very sensitive indicator of any changes in glass phase composition, grain size and microstructural change [12]. Fig. 6 shows the creep deformation curve of low cement castable at 1400 and 1500 °C. At both temperatures, the deformation started after reaching the test temperature and increased with the heating time. After 15 h of heating, the rate of deformation was stabilised. The deformation between 5 and 25 h at 1400 °C was found to be 0.002% and at 1500 °C, 0.023% per h. The high rate of deformation at 1500 °C may be due to a more viscous phase leading to grain boundary displacement. Rendtel et al. [13] observed that the creep of low-cement castable is attributed to deformation processes occurring within

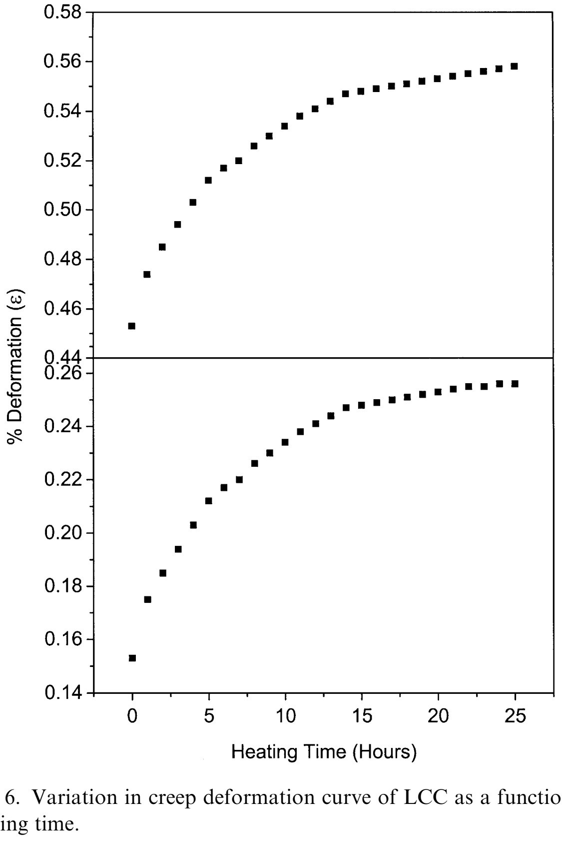


Fig. 6. Variation in creep deformation curve of LCC as a function of heating time.

the inter-aggregate composite, whereas the coarse aggregate particles are considered to be rigid. Similarly, precipitation of fine needles of mullite in the matrix of presently designed LCC as inter-aggregate compound at 1400 °C gives excellent creep resistance. Furthermore, matching of CTE values of inter-aggregate mullite and aggregate mullite influences the hot properties.

The XRD of castable samples heat-treated at 1400 and 1500 °C are shown in Fig. 7. At 1400 °C, anorthite phase was found in addition to mullite and corundum. At 1500 °C, a few calcium hexa-aluminate (CA_6) peaks were also observed. By comparing the XRD phases with strength properties, it can be observed that formation of mullite and anorthite at 1400 °C contributed towards development of CCS, and also influenced the HMOR and creep resistance. Appearance of CA_6 phase above this temperature improved the CCS but adversely affected the HMOR and creep.

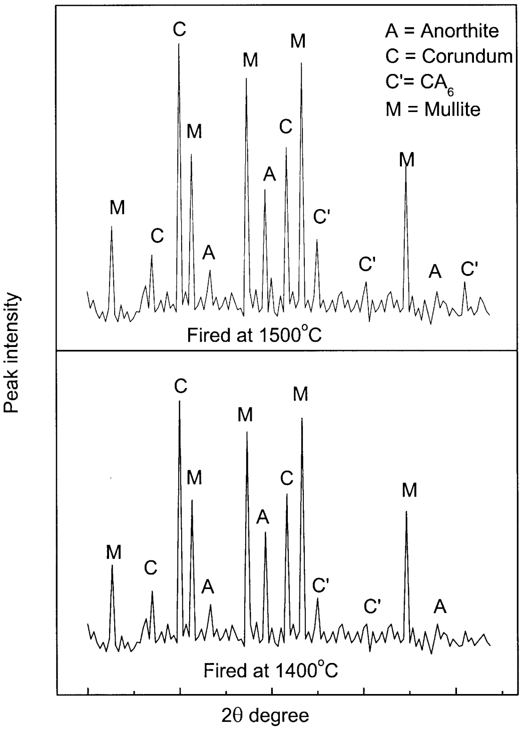
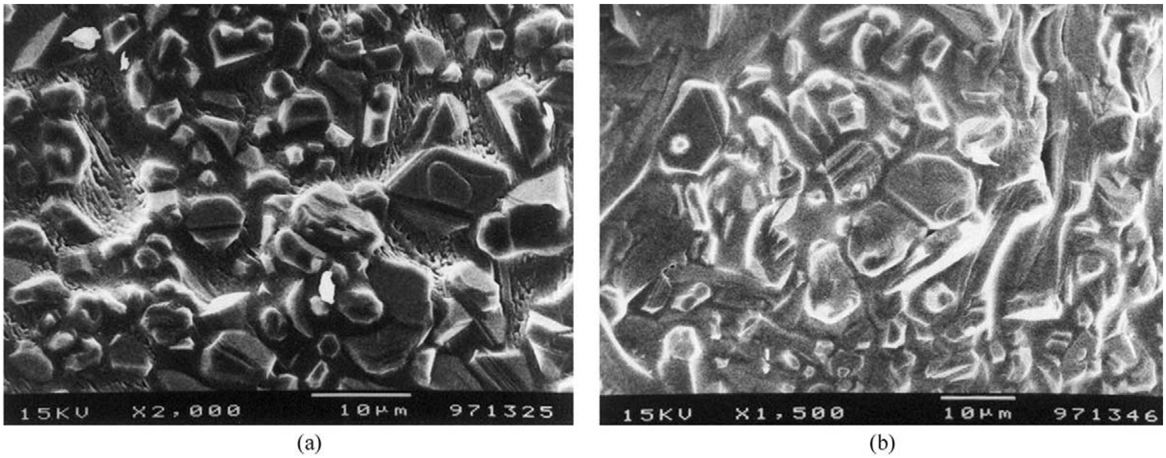


Fig. 7. XRD of LCC fired at 1400 and 1500 °C.

To supplement these observations, SEM of 1400 and 1500 °C fired LCC were carried out and the photomicrographs are shown in Fig. 8(a) and (b), respectively. In 1400 °C fired samples, fine needle shaped crystals are occupying the space between larger grains. EDX analysis confirmed that the composition of these grains was close to mullite. The mullite needles are working as bonded reinforcement to larger grains, leading to a stable structure provided with good HMOR and creep resistance. The majority of open pores is concentrated in the matrix of mullite needles at the tri-junctions of bigger grains. Most of the pores were occupied by the viscous phase at 1500 °C and lead to grain boundary-sliding, causing loss of HMOR and creep resistance. When cooled to room temperature the viscous phases solidified in the pore spaces give rise to a low-porosity structure with excellent CCS.

4. Conclusion

The mullite aggregates synthesised from beach sand sillimanite, exhibits good modulus of rupture, thermal expansion coefficient and refractoriness. The cold crushing strength achievement of LCC above 1200 °C is a result of solidification of viscous phases in the pore spaces, giving reinforcement to the structure. The good HMOR and creep resistance at 1400 °C is influenced by aggregate strength, mullite formation as inter-aggregate compound serving as bonding phase and compatibility of aggregate to aggregate, and aggregate to bond phase in CTE. Reduction of HMOR and creep resistance above this temperature is due to more liquid phase formation, which influenced the grain boundary sliding



(a)

(b)

Fig. 8. (a) SEM of LCC fired at 1400 °C; (b) SEM of LCC fired at 1500 °C.

motion. On the basis of earlier observations, these BSS derived mullite aggregates can be considered suitable for low cement castable applications. However, some more studies are required on the corrosion resistance properties before final conclusion.

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