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Effect of chemical composition on sintering and properties of Al_2O_3–SiO_2 system derived from sillimanite beach sand

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Abstract

Reaction sintering of beach sand sillimanite and alumina is an innovative as well as inexpensive method of mullite formation. Beach sand sillimanite, a by-product generated during the separation of rare earth compounds, and calcined alumina were used as starting materials and were mixed in appropriate proportion and sintered in compacted form at 1500–1575°C. The study reveals that the use of submicron size powder enhances the sintering process. In this investigation, effect of chemical composition on sintering and mechanical/thermomechanical properties has been studied. It was found that the densification process is dependent on the Al_2O_3/SiO_2 ratio. Silica rich composition achieves highest density at 1525°C whereas the alumina rich composition requires 1550°C. Flexural strength measured at room temperature and at 1200°C initially de-creases with alumina content, with a minima at 71–74% Al_2O_3 and then increases again. Microstructure of the sintered is also dependent on the Al_2O_3/SiO_2 ratio of the batch. Mullite made from silica rich composition is needle shape in nature whereas in alumina rich composition they are non-acicular in nature.

1. Introduction

Efforts have been made earlier to develop mullite ceramics by reaction sintering [1–4]. Al_2O_3 containing reactants traditionally used for this purpose are alumina, refractory grade bauxite, clay and in few cases sillimanite group of minerals. A gradual depletion of these naturally occurring high alumina raw materials has made a serious challenge to the refractory industries to keep on continued production of such refractory, that is in high demand. In view of this it has become imperative to find alternate sources of high alumina aggregate. India is one of the few countries in the world that has significant deposits of beach sands. Beach sand sillimanite, a by-product generated in large amount during the separation of rare earth oxide, does not find wide application in refractory industries primarily due to its fineness. The successful use of this material is dependent on aggregate making.

Although a number of authors have studied the thermal transformation of sillimanite to mullite [5,6], the work on beach sand sillimanite is limited.

Sillimanite sand on heating decomposes to mullite and amorphous silica in the temperature range 1500–1650°C depending on the particle size and impurity level.

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

The product quality can be improved by combining the silica released during decomposition of sillimanite by the addition of alumina. The present investigation was carried out to develop mullite/mullite-corundum aggregate from beach sand sillimanite for its commercial utilisation. Thus the mullite/mullite-corundum aggregates were produced by a process of reaction sintering. In this investigation an attempt has been made to study the effect of chemical composition on the densification of SiO_2–Al_2O_3 system derived from beach sand sillimanite and alumina. Attempt has also been made to study the compositional effect on the mechanical/thermomechanical properties and microstructure of the aggregate developed.

2. Experimental

Beach sand sillimanite obtained from Indian Rare Earths Limited (IREL), India and commercial calcined

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alumina obtained from Indian Aluminium Company Ltd. (INDAL), India, were used in this investigation. The particle size distribution of the starting sillimanite powder and calcined alumina were determined in a sedigraph apparatus using calgon as dispersing agent.

The chemical analyses were done by a conventional wet chemical method. Five batch compositions were studied namely S, M, Cl, C2 & C3 having 57.6, 70.54, 73.42, 76.29 and 79.16 wt% alumina, respectively. To enhance the reaction sintering all the batches were attrition-milled in a water medium in a zirconia pot using zirconia ball. The surface area of the milled powder was determined by BET method in a BET apparatus (Sorpty 1750, Carlo Erba, Italy). Surface area of the powders was determined at regular intervals. The optimum milling time is selected by studying the surface area against milling time. The slurries thus obtained were dried at 1105°C, crushed to break the agglomerates, mixed with organic binder and uniaxially pressed at a pressure of 120 MPa. After drying at 110 ± 5°C these samples were fired at a temperature varying from 1500 to 1575°C at an interval of 25°C with a 2 h soaking period. Firing was done in an electric furnace and the heating rate was 5°C min^{-1} up to 1100°C, after that 3°C min^{-1}. up to the final firing temperature. Fired products thus obtained were characterised in terms of linear shrinkage, bulk density, apparent porosity, flexural strength, at room temperature (RT) as well as at 1200°C. Phase identification and microstructural analysis were done by X-ray diffraction study (XRD) and scanning electron microscopy (SEM) and infrared spectroscopy (IR).

Bulk density and apparent porosity of the sintered product were measured by a conventional method using Archimedes' principle in water medium.

Flexural strength at room temperature was determimed by the three point bending method in an apparatus (Instron) with a span length of 40 mm and crosshead speed of 0.5 mm min^{-1} for a test bar of $6 \times 6 \times 50$ mm^3. The samples used were polished and edges were chamfered with a diamond disc. Hot MOR was also determined by the three point bending method at 1200°C.

X-ray diffraction pattern of the raw materials and sintered product were obtained in a diffractometer using Ni-filter and Cu-K_α radiation. Diffraction patterns were recorded in the Braggs angle (2θ) range 15–60°. Microstructure of the sintered product was investigated using sputtered gold coating on the polished surface after chemical (HF) and thermal etching. IR-spectrometer was used to record IR transmission spectra using KBr disc method, and IR transmission was recorded over the wave number range 400 to 4000 cm^{-1}.

Table 1
Chemical composition of the raw materials

Component	Wt%	
	Sillimanite	Alumina
Al_2O_3	57.6	99.3
SiO_2	40.3	—
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	0.02
Phase analysis	Major-sillimanite Minor-quartz, kaolinite	α-alumina

3. Results and Discussion

3.1. Raw material characterisation

The chemical analyses of the raw materials used in this investigation are given in Table 1. Microscopic observation under polarising microscope and XRD study reveal that the mineral present in the sillimanite beach sand is mostly sillimanite associated with small amounts of quartz and kaolinite as impurities. Table 1 shows that SiO_2 content of the sillimanite sand (40.3%) is higher than the stoichiomietric amount.This excess SiO_2 occurs in the sand as quartz which is confirmed from XRD pattern (Fig. 1). The IR pattern of the sillimanite sand is shown in Fig. 2. The absorption peak at 1175 cm^{-1} also clearly indicates that this mineral is sillimanite.

Particle size distribution of the starting sillimanite powder (obtained by vibromilling) and as received commnercial alumina used in this study are shown in Fig. 3. The average particle size of the sillimanite and

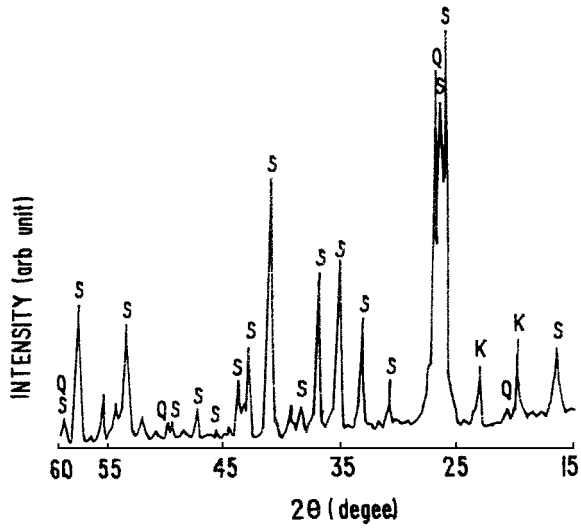

Fig. 1. X-ray diffraction pattern of beach sand sillimanite. S—sillimanite, Q—quartz, K—kaolinite.

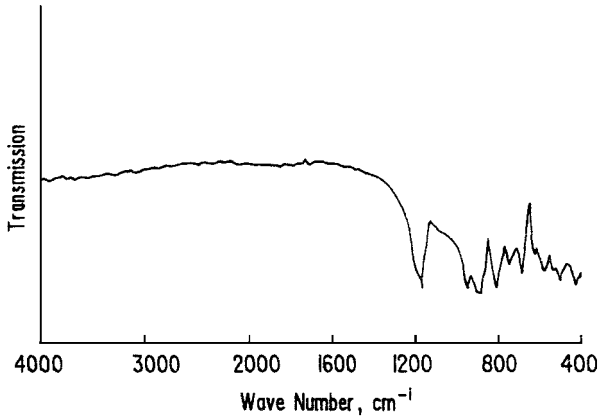

Fig. 2. Infrared transmission spectrum of sillimanite sand.

alumina are 4.5 and 5.0 μm, respectively. Five different batches are selected for this investigation and their composition and sample code are given in Table 2.

All the batches are attriton milled for a definite time period, obtained by studying the variation of specific surface area against milling time. As shown in Fig. 4, the specific surface area increases with milling time up to 9 h and beyond that, although it increases with time, the variation is not appreciable. Hence a optimum milling time of 9 h is chosen for all the batches used in this investigation. Since all the batches are attrition milled for a specific time of 9 h; they have similar particle size distribution which is reflected in the apparent porosity data of the green compact after uniaxial pressing. They are in a close range of 44.2–45%.

3.2. *Effect of chemical composition on densification*

Investigation on the aggregate developed revealed that silica rich mullite aggregate (S) has undergone

Table 2
Batch Composition

Sample Code	Sillimanite	Alumina	AI_2O_3 content in the batch (wt%)
S	200	nil	57.60
M	140	63.00	70.54
Cl	125	76.39	73.42
C2	115	93.44	16.29
C3	100	107.10	79.16

appreciable shrinkage when fired at 1525°C, whereas it is 1550°C for the other composition, as shown in Fig. 5. It was found that the ultimate linear shrinkage at 1575°C is almost the same (16.16–16.39 %) in all the cases irrespective of alumina content. The rate of densification of silica rich composition was relatively high compared to the other composition. The bulk density of the aggregates were directly proportional to alumina content and this trend was observed at all firing temperatures. Fig. 6 indicates that densification behavior is dependent on the alumina content. [7,8] Silica rich composition (S) achieves its highest bulk density at 1525°C. The highest B. D. of mullite composition (M) achieved at 1550°C has the value of 3.16, which is close to the true density of the mullite. Since the sillimanite beach sand contains several impurities, the densification proceeds through liquid phase sintering. It was found that bulk density increases with firing temperature up to a certain level irrespective of the Al_2O_3 content. Beyond this temperature it decreases due to the excessive formation of vitreous phase and closed pores. Apparent porosity data also supports the above observation.

The XRD pattern of sillimanite and mullite is very close, and it is very difficult to measure mullite content of the batches quantitatively by this method. However, infrared technique may be used to distinguish sillimanite

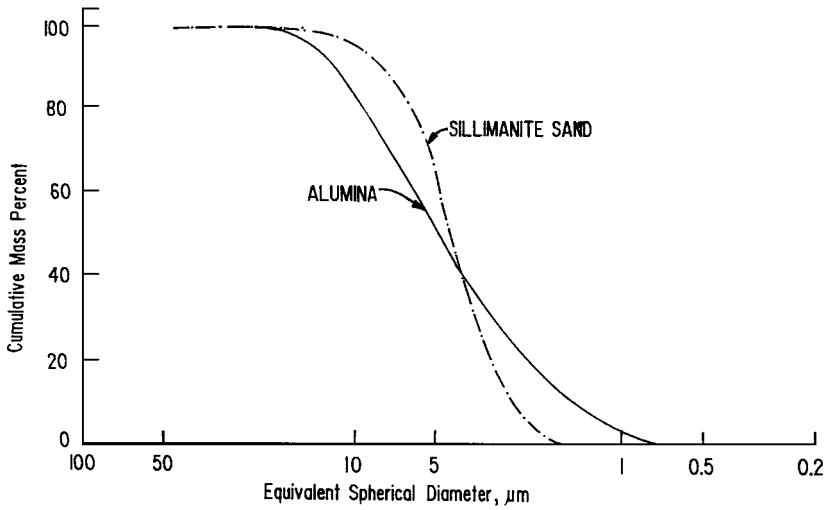

Fig. 3. Particle size distribution of the starting raw materials.

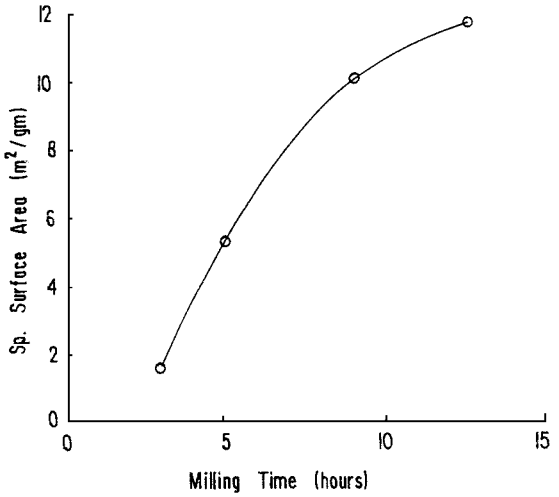

Fig. 4. Effect of milling time on the specific surface area of the batch.

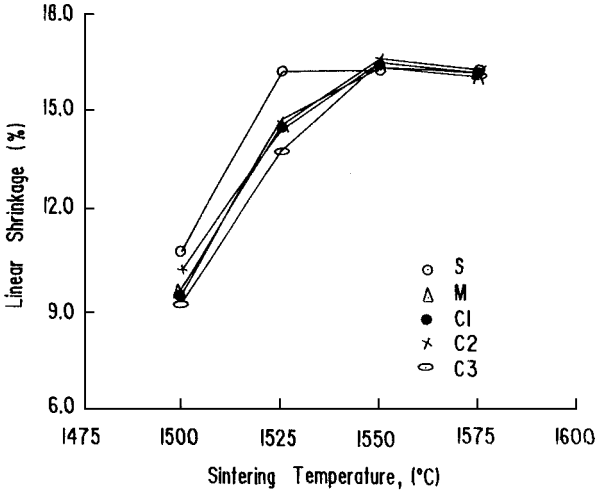

Fig. 5. Variation of linear shrinkage with sintering temperature.

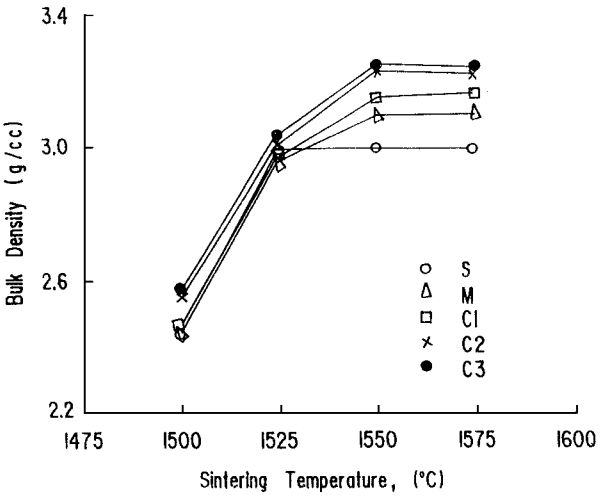

Fig. 6. Effect of sintering temperature on the bulk density of the samples.

and mullite in the fired product [9,10]. Even Roy et al. [11] show that it is possible to determine quantitatively the unreacted sillimanite in the sintered product. IR pattern of the sintered body is shown in Fig. 7. The total absence of the characteristic sillimanite absorption peak at 1175 cm^{-1} in all the compositions fired at 1525°C clearly indicates complete conversion of sillimanite to mullite at this temperature. Hence XRD together with IR technique are used to identity the crystalline phases in the fired product.

3.3. Microstructure

All the samples except S achieves their highest bulk density at a firing temperature of 1550°C. Microstructural evaluation were done on these samples. Scanning electron photomicrograph of the samples S, M, Cl, C2, C3 fired at 1550°C /2 h are shown in Fig. 8. In S sample the mullite crystals with orthorhomibic habit of sillimanite was found. The black voids in the micrograph are due to the dissolution of the silicate phase in HF during chemical leaching as shown in Fig. 8(a). Addition of Al_2O_3 into the batch reduces the silicate phase as a result of mullite formation. The resulting microstructures are in compact form with a higher degree of grain to grain interlocking as shown in Fig. 8(b)–(e). In all the cases mullite crystals retains the crystalline habit of sillimanite, some non-acicular or pallets of mullite were found in the alumina rich sample C2 and C3. Some earlier workers also reported such findings [12]. Intergranular Vitreous phase is less in Cl composition and higher on either side of this. Table 4 also supported the same result. In samples C2 and C3 the hexagonal crystals of corundum were evenly distributed within the mullite matrix.

3.4. Strength

Flexural strength at room temperature of the aggregates as a function of alumina content and sintering

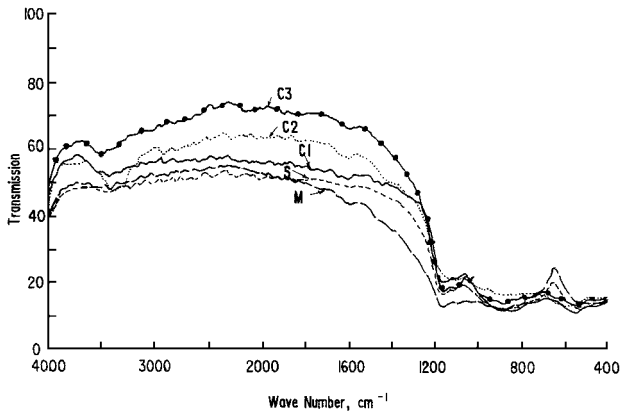

Fig. 7. IR pattern of the samples sintered at 1525°C/2 h.

temperature are shown in Fig. 9. Each aggregate develops highest room temperature flexural strength at 1550°C. Strength of silica rich aggregate (S) was maximum at all temperatures and a maximum strength of 161 MPa was observed for "S" composition fired at 1550°C. At all firing temperatures the curves show a minima around mullite composition "M", and it is higher on either side of this. Thus the flexural strength at room temperature is very much dependent on the Al_2O_3/SiO_2 ratio.

High temperature flexural strength (at 1200°C) was also found to be dependent on the Al_2O_3/SiO_2 ratio and

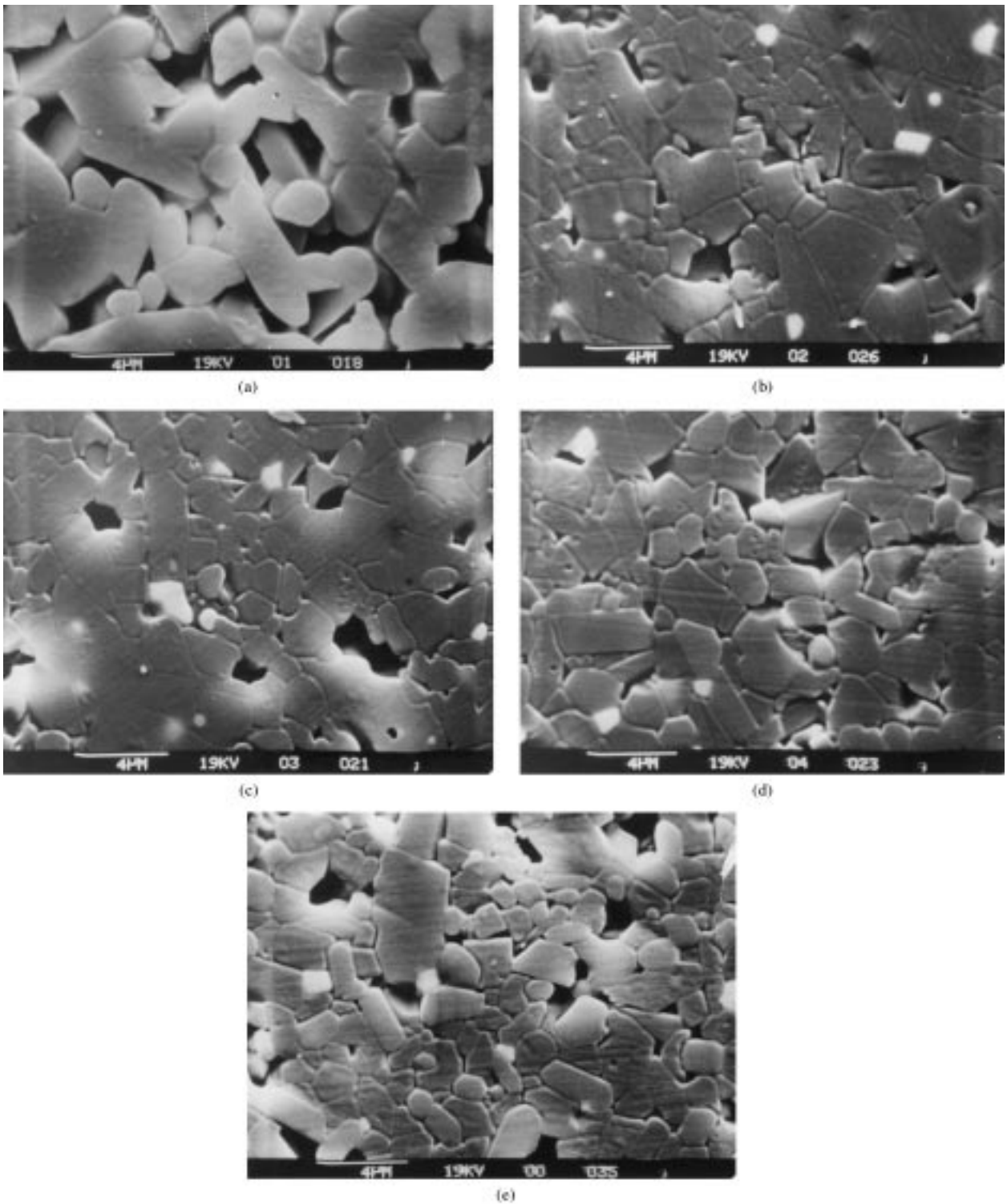

Fig. 8. Scanning electron micrographs of the samples sintered at 1550°C: (a) sample S, (b) sample M, (c) sample C1, (d) sample C2, (e) sample C3.

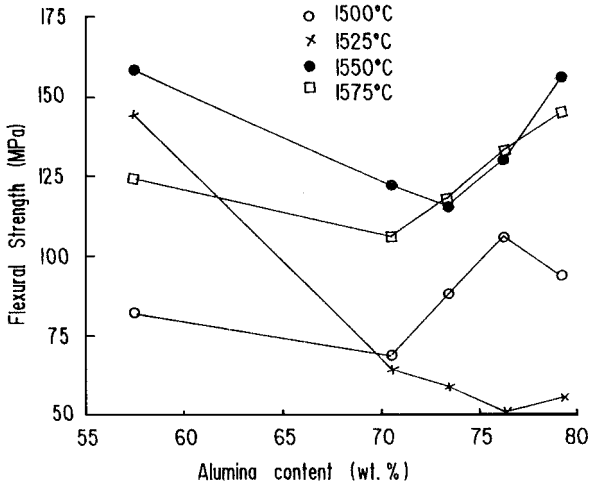

Fig. 9. Variation of room temperature flexural strength with chemical composition of the samples sintered at different temperatures.

firing temperature (Fig. 10). At all sintering temperature the flexural strength at 1200°C of silica rich composition (S) was maximum. At high temperature, softening of the glassy phase occurs, which is responsible for stress relaxation at the crack tips, consequently increasing the HMOR [13]. The highest hot strength of 316 MPa was observed for "S" composition when fired at 1525°C. But in "C" composition that allows sufficient corundum grains in the sintered body shows an increasing tendency in the hot strength at a sintering temperature of 1575°C. Fig. 10 shows that the high temperature flexural strength at 1200°C initially decreases with Al_2O_3 content where there was lower amount of glassy phase and then again increases with Al_2O_3 content.

Glassy phase present in the sintered product (1575°C) was estimated by HF leaching technique [14], the results indicate (Table 3) that the glassy phase is also dependent on the composition. It is minimum"C1"composition

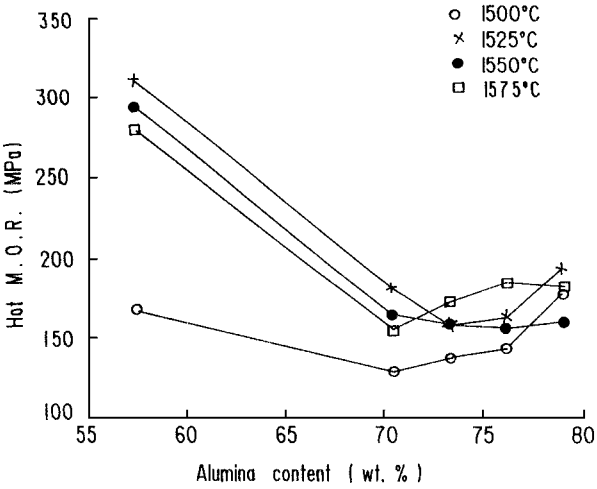

Fig. 10. Effect of Al_2O_3 content on the flexural strength at 1200°C of the samples sintered at different temperatures.

Table 3
Silicate phase content of the product sintered at 1575°C

Sample	Al_2O_3 content (wt%)	Silicate phase content (wt%)
S	57.60	21.64
M	70.54	12.51
Cl	73.42	9.17
C2	76.29	11.98
C3	79.16	15.83

(73.42 %Al_2O_3) and higher on either side of this composition. Higher percent of glass in "M" composition is probably due to the incomplete mullitisation of the silica released during thermal decomposition of sillimanite sand. The alkali content increases with the addition of alumina and this is responsible for increased glassy phase in case of alumina rich composition. High temperature flexural strength is related to this glassy phase content, although the variation is not too high in alumina rich composition.

4. Conclusion

The reaction sintering of beach sand sillimanite and calcined alumina has shown encouraging results when microfine particles were used (specific surface area 10.1 $m^2 gm^{-1}$). Densification of the system and properties of the sintered products are dependent on the alumina/silica ratio. All the compositions achieve their highest bulk density at 1550°C. Silica rich composition in sintered form had relatively high cold and hot flexural strength at 1200°C compared to all other compositions. High temperature flexural strength at 1200°C of compositions containing alumina in the range 71–74 % are lower than those with other alumina contents on either side of this. Mullite formed from sillimanite sand retains the crystal habit of sillimanite during thermal transformation. Non-acicular or pallet mullite were observed in alumina rich composition. Mullite compositions develop a compact microstructure with interlocking orthorhombic mullite crystals.

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