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Synthesis and Mechanical Properties of Mullite from Beach Sand Sillimanite: Effect of TiO_2

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Abstract

Reaction sintering of beach sand sillimanite and calcined alumina is an innovative as well as cost effective method of mullite formation. In the present investigation, beach sand sillimanite and calcined alumina in microfine state were used as starting materials to develop high alumina aggregates for refractories applications using titania additive (0–6 wt%). The raw materials and additive (TiO_2) were mixed in definite proportion and sintered in compacted form at 1400–1550°C with 2 h soaking. It was determined that, alumina/silica ratio of the batch controls densification, flexural strength and microstructural development of the aggregates. Aggregates with almost zero porosity were developed at a sintering temperature of 1500°C with the help of titania additive. Gradual addition of TiO_2 up to 4 wt% promotes the densification process, however, TiO_2 affects the high temperature flexural strength of the aggregates. Aggregates developed from sillimanite sand at 1500°C indicates that the mullites formed are not ideal 3:2 type, but are 1:1 type. Mullite formed in the silica rich composition is long and elongated in nature. At the densification temperature of 1500°C up to 3·06 wt% TiO_2 enters into the mullite structure as solid solution.

1 Introduction

Reaction sintering of Al_2O_3 and SiO_2 bearing materials is a low cost method of mullite formation. The temperature and rate of mullite formation depends on the starting material, particularly on the Al_2O_3 and SiO_2 reactants used, their chemical purity and particle size distribution.[1–6] The common SiO_2 and Al_2O_3 containing reactants used are Al_2O_3 and SiO_2 powder, refractory grade bauxite, clay and gibbsite. Earlier investigation[6] has shown that use of submicron powder having high surface energy and fast heating rate favors mullite formation at relatively lower temperature (< 1600°C). Due to gradual depletion of good quality naturally-occurring deposits of these high alumina raw materials, it has become imperative to find out alternate source of high alumina aggregates to maintain the continued production of such refractories. India is one country with sufficient deposits of beach sand with estimated reserves of sillimanite beach sand of about 54 million tonnes. Beach sand sillimanite, a by product generated during the extraction of rare earth compounds, does not find wide industrial application, mainly due to its fineness (95 wt% passes through 60 mesh BS sieve). Sillimanite beach sand is a potential raw material for use in refractory grain aggregates. This work was undertaken to convert the waste by-product sillimanite sand to synthetic high alumina aggregate, a value added item in the refractory industries.

Sillimanite decomposes to mullite and silica on heating in the temperature range 1300–1700°C.[7] Decomposition temperature depends on the particle size and impurity level of the raw material.

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

The silica formed during this thermal transformation partially reacts with impurities to form a vitreous silicate phase which impairs the quality of the product by deteriorating the high temperature properties like Hot MOR, thermal shock resistance of the products. The product quality can be improved by adding an appropriate amount of alumina to the batch so that the silica released reacts with the alumina to form mullite. Although a number of workers studied the thermal transformation of

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sillimanite to mullite,[7–9] the investigation on beach sand sillimanite is limited. Hence, the present investigation was undertaken to develop mullite/mullite-corundum aggregates from beach sand sillimanite for its commercial utilisation. Thus mullite/mullite-corundum aggregates were synthesised from sillimanite beach sand and alumina by a reaction sintering route. In this study an attempt has been made to study the effect of chemical composition on the densification behaviour of the SiO_2–Al_2O_3 system derived from sillimanite beach sand. An attempt is also made to study the effect of TiO_2 on the densification behaviour and mechanical/thermo-mechanical properties of the aggregates and its microstructure. The compositions of the crystalline mullite phase were studied by Energy Dispersive X-ray (EDX) analysis to correlate the microstructure and properties.

2 Experimental

The major raw materials used in this investigation were beach sand sillimanite and calcined alumina. Beach sand sillimanite was obtained from Indian Rare Earths Limited (IREL) from their Chattrapur plant in Orissa, India and calcined alumina from Indian Aluminium Company Ltd. (INDAL), India. Particle size distribution of the sillimanite powder (obtained by vibromilling) and alumina were determined by sedigraph apparatus using calgon as dispersing agent. Chemical analyses of both the raw materials were done by conventional wet chemical methods. Three batch compositions were selected namely ‘S’, ‘M’ and ‘C’ with 57·6, 71·8 and 80·75 wt% alumina, respectively (in Al_2O_3/SiO_2 ratio). To promote the densification process, 2–6 wt% TiO_2 (rutile) was used as additive in this study.

To enhance the reaction sintering, all the batches were attrition-milled in water medium, in a zirconia pot using zirconia balls for a specified time period. The surface area of the milled powders were determined by BET method in an BET apparatus (Sorpty 1750, Carlo Erba, Italy). Optimum milling time was determined by studying the effect of milling time on the specific surface area. Slurries thus obtained were dried at $110 \pm 5°C$, powdered to break the agglomerate, mixed with organic binder and uniaxially pressed at 100 MPa followed by cold isostatic pressing at 175 MPa. Again after drying at $110 \pm 5°C$, these green samples were fired at 1400–1550°C with 2 h soaking time. Firing was done in an electric furnace and the heating rate was 5°C min^{-1} upto 1100°C and 3°C min^{-1} up to the final firing temperature. Fired products thus obtained were characterised in terms of bulk density, flexural strength at high temperature (1200°C), microstructure and phase assembly.

Bulk density and apparent porosity of the green as well as sintered product were determined by conventional liquid displacement method using Archimedes Principle in xylene and water medium, respectively.

Hot modulus of rupture were determined by standard three point bending method in an instrument with span length of 43 mm using sintered bars having dimension 55×5×5 mm. The samples used were polished and edges were chamfered with diamond disc. Hot MOR were determined after a dwelling period of 30 min at 1200°C.

X-ray powder diffraction pattern of the raw materials and fired products were obtained in an X-ray diffractometer using nickel filtered Cu-K_α radiation. Diffraction patterns were recorded for the 2θ range 15–60°. IR-Spectrometer was used to record IR transmission, using KBr disc method in the wave number range 400–4000 cm^{-1}, Microstructural analysis and phase identification were done by scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis using sputtered carbon coating on the polished surface of the sintered samples after thermal etching.

3 Results and discussion

3.1 Raw material characterisation

The chemical analyses of the raw materials used in this investigation, i.e. sillimanite sand and calcined alumina are given in Table 1. X-ray diffraction study (Fig. 1) clearly indicates that beach sand sillimanite mainly consists of sillimanite mineral associated with small amount of mineral impurities like, quartz, kaolinite. Infrared spectra pattern of the sillimanite sand is shown in Fig. 2. The absorption peak at 1175 cm^{-1} is characteristic of sillimanite.[9] The silica content of the sillimanite sand is higher than the stoichiometric amount and this excess silica occurs in the minerals as quartz as shown in Fig. 1. The alumina used in this investigation was commercial calcined alumina consisting of only α-Al_2O_3. The particle size distribution of

Table 1. Chemical composition of the raw materials

Constituents (wt%)	*Sillimanite sand*	*Calcined alumina*
SiO_2	40·30	—
Al_2O_3	57·60	99·30
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	—

the starting raw materials are given in an earlier reference.[9] The average particle size of the vibro-ground sillimanite powder was 4·5 μm and calcined alumina was 5·0 μm. Figure 3, indicate the variation of specific surface area of the milled powder with the milling time. From this figure it is clear that the sp. surface area increases with the milling time up to 9 h, after that although it varies with time, the variation is not significant. Hence an optimum milling time of 9 h was selected for all the batches in this investigation. Twelve different batches were studied in this investigation and their composition and sample code used to identify them are given in Table 2.

Since all the batches are attrition milled for 9 h they have got similar particle size distribution after milling, which is reflected in the apparent porosity data of the green bars after isostatic pressing, all in the range 40–42 vol%.

3.2 Densification

The reaction sintering in this study is not of pure materials, but of sillimanite sand containing many impurities and α-alumina. In this process the chemical reaction of the starting materials and densification of the compacts takes place in a single step. In the reaction sintering mechanism densification and chemical reaction compete each other. In pure materials high degree of densification is preferred prior to mullitisation, but this may not be needed here since the impurities probably aid liquid formation.

Densification behaviour is shown in Fig. 4 TiO_2 added as additive into the batch promotes

Table 2. Batch composition selected and sample codes used for the study

Sample code	*Sillimanite sand (wt%)*	*Calcined alumina (wt%)*	*Additive*	*Additive content (wt%)*
Sillimanite Composition				
S	100·00	—	Nil	—
ST2	98·00	—	TiO_2	2·00
ST4	96·00	—	TiO_2	4·00
ST6	94·00	—	TiO_2	6·00
Mullite Composition				
M	68·97	31·03	Nil	—
MT2	67·59	30·41	TiO_2	2·00
MT4	66·21	29·79	TiO_2	4·00
MT6	64·83	29·17	TiO_2	6·00
Alumina Rich Composition:				
C	48·29	51·71	Nil	—
CT2	47·32	50·68	TiO_2	2·00
CT4	46·35	49·65	TiO_2	4·00
CT6	45·39	48·61	TiO_2	6·00

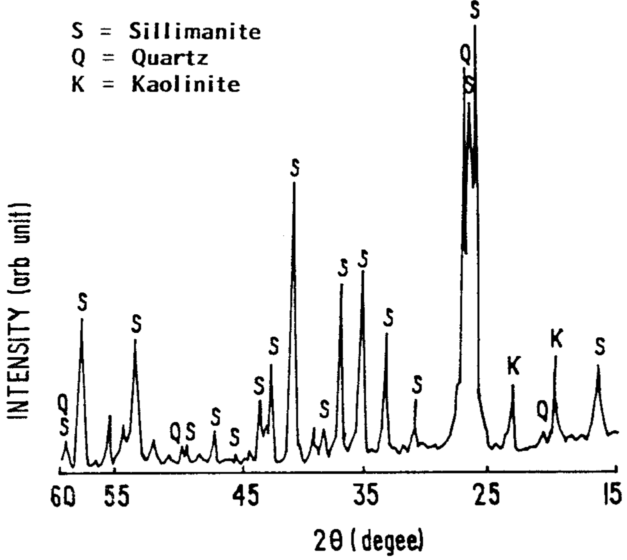

Fig. 1. X-ray diffraction pattern of the sillimanite beach sand showing the peak of quartz (Q) and kaolinite (K) as impurities.

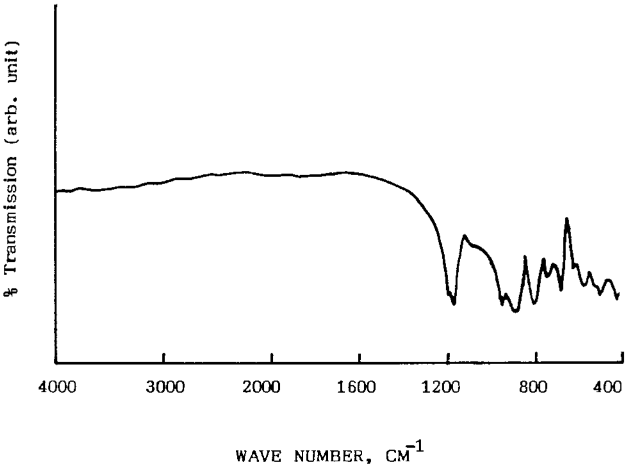

Fig. 2. Infrared spectra of the sillimanite sand.

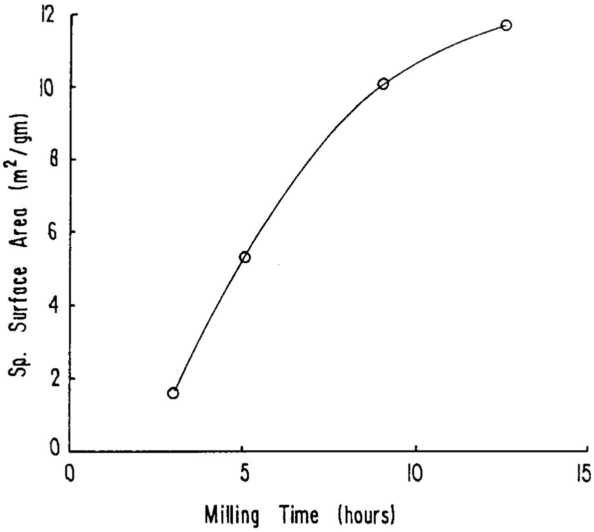

Fig. 3. Effect of milling time on the specific surface area of the milled batches.

densification process by two ways (i) it increases the cation mobility by the formation of cation vacancy resulting from the substitution of Al^{+3} by Ti^{+4}; and (ii) forming a liquid phase at the firing temperature, which increases the diffusion or mass transport of reactants through it. From Fig. 4, it is clear that sillimanite composition (S) due to its higher silica content requires only 2 wt% TiO_2 to achieve the maximum bulk density of 3·00 g^{-1} cc at 1500°C/2 h. Four wt% TiO_2 even decreases this temperature to 1450°C, where as M and C composition due to their higher Al_2O_3 content requires 4 wt% TiO_2 to lower the densification temperature to 1500°C. The particle rearrangement due to the formation of liquid phase helps to remove the pore from the grain boundaries. However beyond this range the properties deteriorate in all the cases due to higher liquid content. The bulk density is directly proportional to the alumina content. In all compositions the bulk density initially increases with sintering temperature up to a certain level irrespective of the titania content, beyond this temperature it decreases due to excessive amount liquid formation. Bloating surface of the sample fired at >1500°C also confirms this. From this investigation it was found that, in case of sillimanite sand itself, 2 wt% TiO_2 and a firing temperature of 1500°C was optimum to develop aggregate with high bulk density and almost zero porosity. But when alumina is added in to the batches (M and C) they need a still higher wt% of TiO_2 (4%) to develop high alumina aggregate at 1500°C. In the case of M composition, the maximum bulk density achieved is 3·11 g^{-1} cc at 1500°C with 4 wt% TiO_2 compared to that of mullite is 3·16 g^{-1} cc.

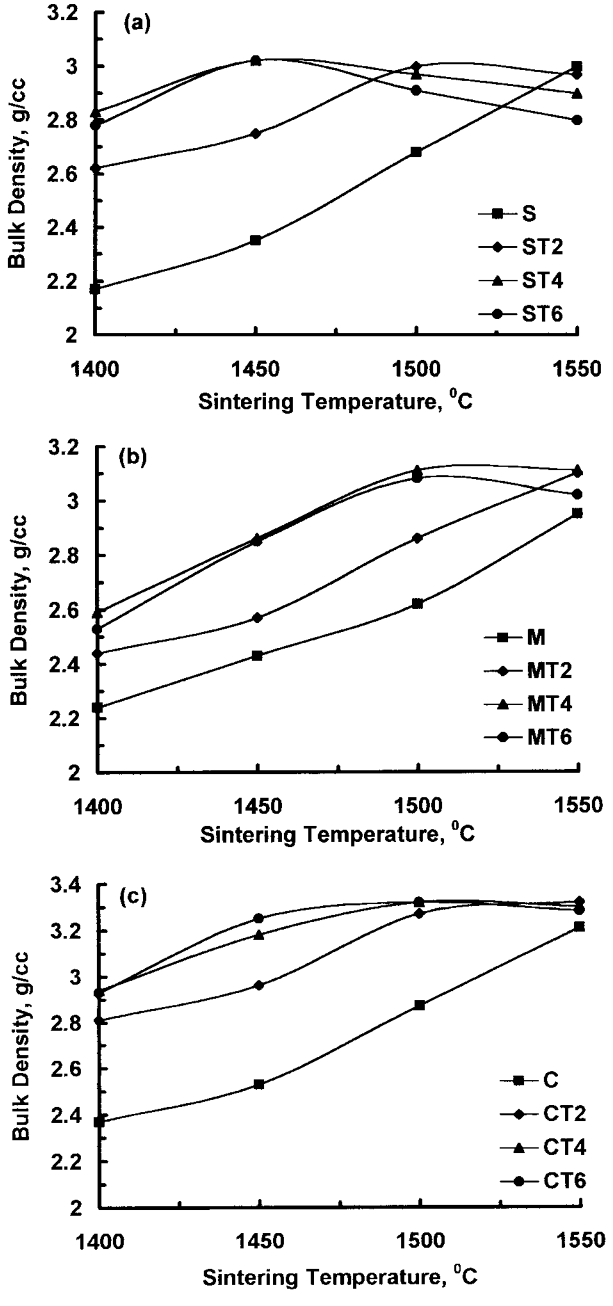

Fig. 4. Variation of bulk density of the sample containing TiO_2 additive with sintering temperature: (a) sillimanite composition; (b) mullite composition; (c) alumina rich composition.

3.3 Microstructure

Since except S, all the composition achieves their highest bulk density (~99% of the theoretical density) with 4 wt% TiO_2 and at a firing temperature of 1500°C, these samples were selected for microscopic observation and phase identification. Samples ST4 and ST2 were also investigated for comparison purposes. X-ray diffraction of these samples with 4 wt% TiO_2 and sintered at 1500°C are shown in Fig. 5. Since it is very difficult to identify mullite phase in the sintered product due to the close similarity in the XRD pattern of sillimanite and mullite, IR spectroscopy was used to identify the mullite formation.[10–12] Figure 6 shows the IR transmission pattern of these sintered samples, in all the cases the nonexistence of the characteristic sillimanite absorption peak in the vicinity of 1175 cm^{-1} clearly indicates the near to complete conversion of sillimanite to mullite. The crystalline phases present in the aggregates is mullite in S and M composition, mullite and corundum in C composition. No crystalline SiO_2 phases were found in any composition with or without TiO_2. Silica released during the thermal decomposition of sillimanite is either amorphous in nature or form a liquid phase by reacting with impurities, at the sintering temperature. Some earlier worker also found such observation.[7]

Microstructure of the sintered samples was also related to alumina to silica ratio. Scanning electron photomicrograph of the samples ST2, ST4, MT4 and CT4 fired at 1500°C were shown in Fig. 7. In alumina rich samples there was an evidence of large grain size, and the mullite formed is non accicular in nature. The structure of silica rich samples (ST2 and ST4) shows the uniform distribution of glassy phase with in the matrix. [Figs 7(a) and (b)]. Study shows that ST4 contains a higher amount of intergranular vitreous phase than ST2. Since these samples contains higher

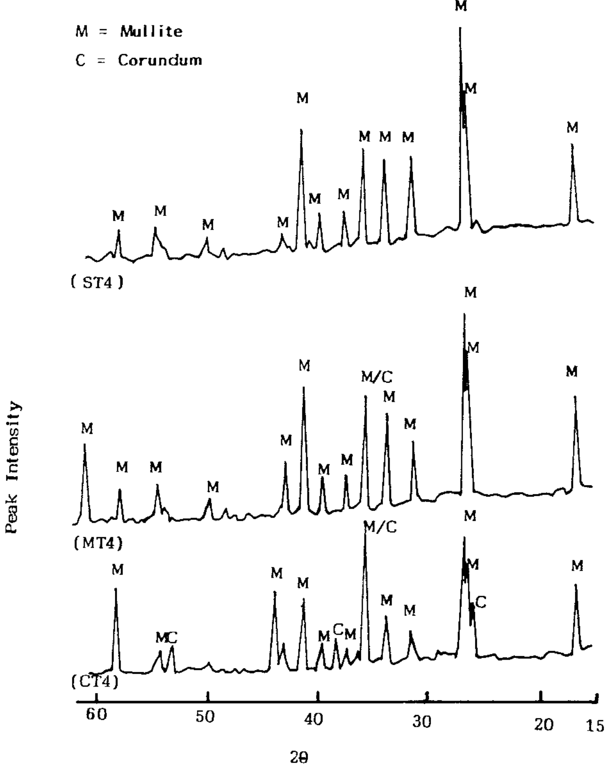

Fig. 5. XRD pattern of the samples ST4, MT4 and CT4 fired at 1500°C/2 hrs.

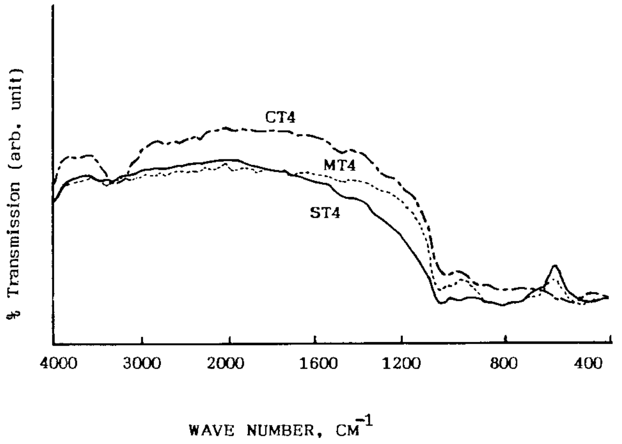

Fig. 6. IR absorption spectra of the samples ST4, MT4 and CT4 sintered at 1500°C, showing the absence of characteristic sillimanite absorption peaks.

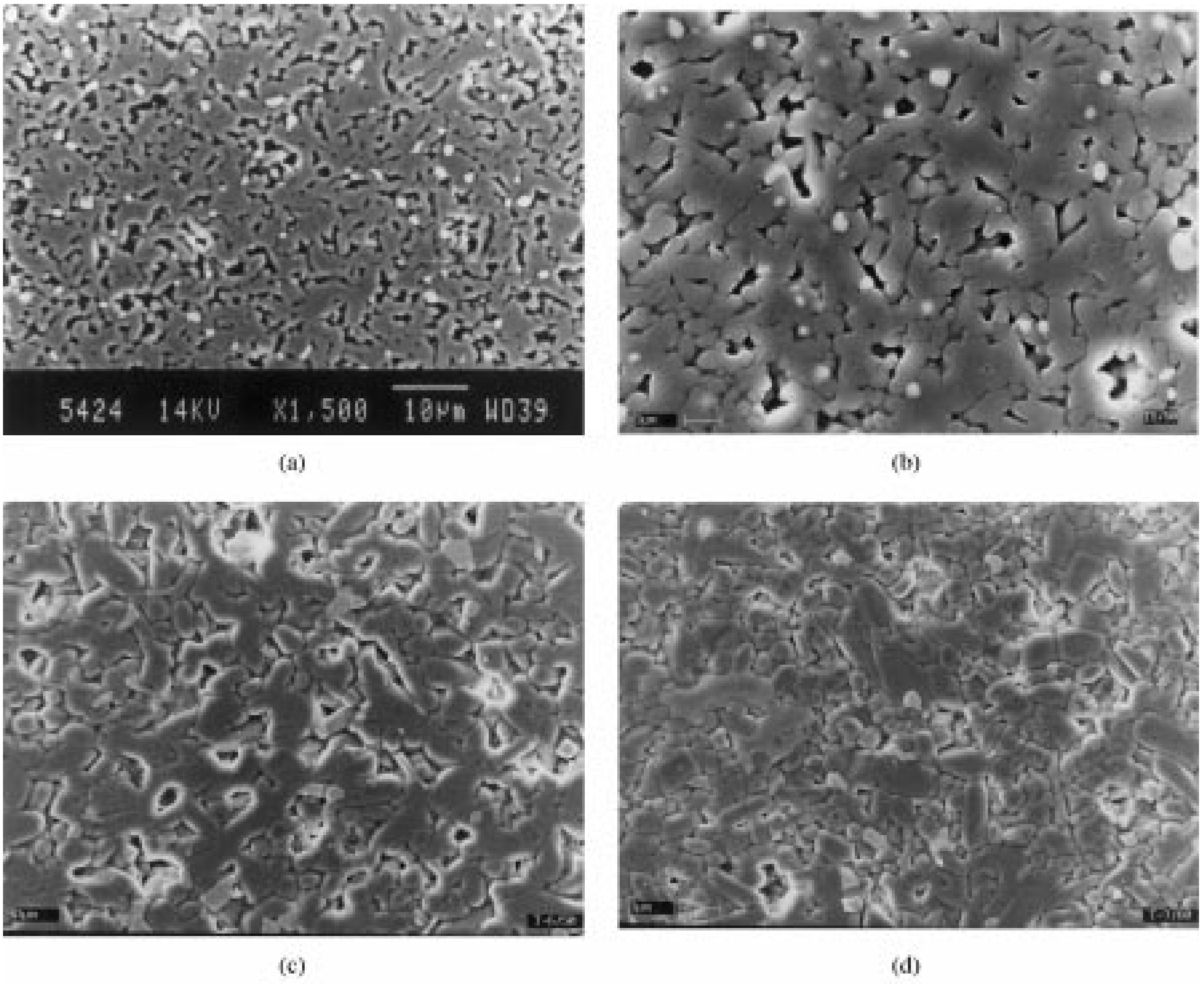

Fig. 7. Scanning electron photomicrograph of the samples fired at 1500°C/2 h. (thermal etching): (a) ST2, (b) ST4; (c) MT4; and (d) CT4.

amount of silica densification mainly proceeds by liquid phase sintering, and the mullite formed in these samples (ST2 and ST4) are needle shaped in nature. Figure 7(C) indicates that MT4 microstructure is compact with a higher amount of grain to grain interlocking with very small amount of vitreous phase. In CT4 the glassy phase and grain size is higher than in MT4. The higher vitreous phase is due to the extra alkali entered into the batch from commercial calcined alumina. Some non acicular mullite and hexagonal plate like corundum were observed particularly in CT4.

Energy dispersive X-ray analysis of the mullite grain indicate that the Al_2O_3/SiO_2 ratio in the mullite grains were in the range of 0·8496–0·9496 and it is not ideal 3:2 mullite and at 1500°C up to 3·06 wt% of TiO_2 added as additive enters in to mullite grain due to solid solution formation. Hence ultimately most of the additives enters in to the solid solution with mullite with a very small amount in the intergranular vitreous phase. The elemental analysis in terms of oxides of the mullite grains were shown in Table 3.[13,14]

3.4 Strength

High temperature mechanical strength is a decisive parameter of any high alumina ceramics. The effect of sintering temperature and additive (TiO_2) contents on the high temperature flexural strength at 1200°C is shown in Fig. 8. From Fig. 8 it is seen that the high temperature strength of the samples is dependent on the chemical composition or Al_2O_3/SiO_2 ratios.[15–17] The sillimanite composition (S) shows the highest flexural strength at 1200°C followed by mullite composition and alumina rich composition. The highest hot strength of sillimanite composition is due to the stress relaxation at the crack tips by softening of the glassy phase at this temperature.[6] The composition (C) which allows sufficient corundum phase in the sintered products, shows a very small change in hot strength with sintering temperature (~40%). The additive affects the high temperature strength due to excessive formation of glassy phases. In all compositions, except ST2, the hot MOR decreases with the wt% of additives and this trend was observed particularly at higher sintering temperature. The highest flexural strength of >400 MPa was observed in ST2 fired at 1500°C/2 h. In all compositions beyond a certain percentage of TiO_2 (2 wt% for S and 4 wt% for M and C) the hot MOR falls rapidly due to the formation of excessive glassy phase, open pores (bloating) and inhomogenity in the microstructure of the sintered product. Since in ST2 samples fired at 1500°C for 2 h, out of 2 wt% TiO_2 added in to the batch, 1·99 wt% additive (with respect to batch) enters in to the solid solution in the mullite grain, without changing the composition or amount of vitreous phase, it shows the highest flexural strength at 1200°C

Table 3. Composition of mullite grains of the samples fired at 1500°C/2 h.

Sample no.	*Wt%*			*Al_2O_3/SiO_2*
	Al_2O_3	*SiO_2*	*TiO_2*	
ST2	59·09	40·91	1·99	0·8496
ST4	56·68	40·67	2·66	0·8198
MT4	59·86	37·08	3·06	0·9496
CT4	59·11	38·11	2·78	0·9124

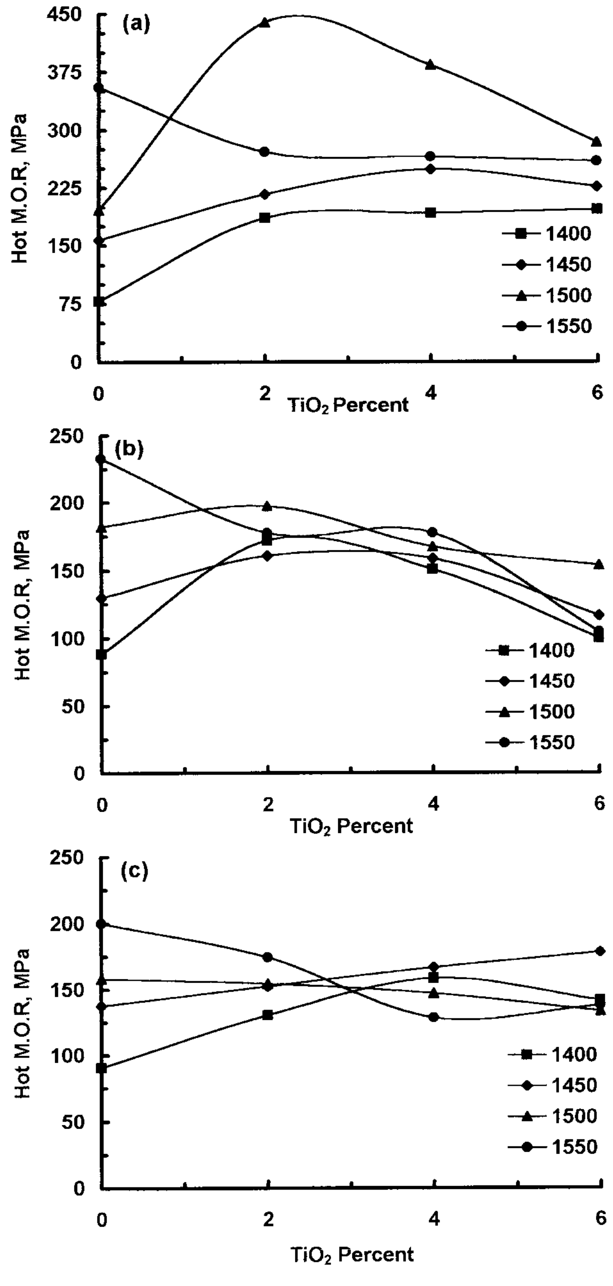

Fig. 8. Variation of hot MOR at 1200°C of the samples with TiO_2 content at different sintering temperature: (a) sillimanite composition; (b) mullite composition; (c) alumina-rich composition.

(> 400 MPa). All other composition shows lower MOR due to higher amount, and change in composition of the vitreous phase.

4 Conclusion

Reaction sintering of microfine beach sand sillimanite and calcined alumina is an inexpensive as well as innovative method of mullite formation. Sintering of sillimanite beach sand as such at high temperature (> 1600°C) is difficult and may not be economically viable. Densification at lower temperature was achieved by lowering the particle size by wet milling. Addition of TiO_2 lowers the densification temperature and it was found from this study that 4 wt% TiO_2 is the optimum to lower the densification temperature to 1500°C, without much deterioration(~25%) in the high temperature properties, although the high temperature flexural strength is dependent on the additive content. X-ray and IR study confirms the near to complete conversion of sillimanite to mullite at 1500°C in the presence of 4 wt% TiO_2 additive. The mullite developed is not ideal 3:2 mullite and at the densification temperature of 1500°C up to 3·06 wt% of TiO_2 enters into the mullite structure by solid solution formation.

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References

1. Aksay, I. A., Dabbs, D. M. and Sarikaya, M., Mullite for structural, electronic, and optical applications. *J. Am. Ceram. Soc.*, 1991, **74**, 2343–2358.
2. Nurishi, Y. and Pask, J. A., Sintering of α-Al_2O_3/amorphous silica compacts. *Ceram. Int.*, 1982, **8**, 57–59.
3. Saruhan, B., Albers, W., Schneider, H. and Kaysser, W. A., Reaction and sintering mechanisms of mullite in the system cristobalite/α-Al_2O_3 and amorphous SiO_2/α-Al_2O_3. *J. Eur. Ceram. Soc.*, 1996, **16**, 1075–1081.
4. Rana, A. P. S., Aiko, O. and Pask, J. A., Sintering of α-Al_2O_3/quartz and α-Al_2O_3/cristobalite related to mullite formation. *Ceram. Int.*, 1982, **8**, 151–153.
5. Rodrigo, P. D. D. and Boch, P., High purity mullite ceramics by reaction sintering. *Int. J. High Tech. Ceram.*, 1985, **1**, 3–30.
6. Boch, P., Chartier, T. and Rodrigo, P. D. D., High purity ceramics by reaction sintering. In *Ceramic Transaction 6: Mullite and Mullite Matrix Composites*, ed. S. Somiya, R. F. Davis, and J. A. Pask. American Ceramic Society, Westerville, OH, 1990, pp. 353-374.
7. Schneider, H. and Majdic, A., Preliminary investigation on the kinetics of high temperature transformation of sillimanite to 3/2 mullite plus silica and comparison with the behaviour of andalusite and kyanite. *Sci. Ceram.*, 1981, **11**, 191–196.
8. Wilson, H. H., Mullite formation from sillimanite group of minerals. *Amer. Ceram. Soc. Bull.*, 1969, **48**(b), 796–797.
9. Navale, A. S., Rao, N. K., Chakravarty, S. P., Bhat, R. and Roy, S. K., Analysis of mineral transformation by infrared spectroscopy: sillimanite to mullite. In *Proc. 5th National Symp., Analytical Spectroscopy Including Hyfenated Techniques*, eds. M. D. Shastry and A. G. Page, Ind. Anal. Chemistry, Bombay, 1988, pp. 115–119.
10. Tripathi, H. S. and Banerjee, G., Effect of chemical composition on sintering and properties of Al_2O_3–SiO_2 system derived from sillimanite sand. *Ceram. Int.*, 1998, in press.
11. Chaudhury, S. P., The distinction between mullite and sillimanite: a review. *Interceram.*, 1981, **3**, 199–202.
12. Roy, R. and Francis, E. E., On the distinction of sillimanite from mullite by infrared technique. *Amer. Miner.*, 1953, **38**, 725–728.
13. Murthy, M. K. and Hummel, F. A., X-ray study of the solid solution of TiO_2, Fe_2O_3 and Cr_2O_3 in mullite ($3Al_2O_3.2SiO_2$). *J. Am. Ceram. Soc*, 1960, **43**, 267–273.
14. Chaudhuri, S. P., The solid solution in mullite. *J. Canadian Ceram. Soc.*, 1960, **58**(1), 61–76.
15. Schneider, H., Okada, K. and Pask, J. A., *Mullite and Mullite Ceramics*. John Wiley and Sons Ltd., Chichester, UK., 1994, pp. 199–232.
16. Sacks, M. D. and Pask, J. A., Sintering of mullite containing materials I. Effect of chemical composition. *J. Am. Ceram. Soc.*, 1982, **65**(2), 65–70.
17. Kanzaki, S., Tabata, H., Kumazawa, T. and Ohta, S., Sintering and mechanical properties of stoichiometric mullite. *J. Am. Ceram. Soc.*, 1985, **68**, C6.