ELSEVIER

Ceramics International 26 (2000) 1–6

CERAMICS INTERNATIONAL

Thermal shock behaviour of high alumina aggregates derived from sillimanite beach sand with and without Fe_2O_3 doping

H.S. Tripathi*, Swapan Kr Das, G. Banerjee

Central Glass & Ceramic Research Institute, Refractory Division, 196 Raja S.C. Mullick Road, Calcutta-700 032, India

Received 1 October 1998; received in revised form 28 October 1998; accepted 7 December 1998

Abstract

In this investigation, three types of high alumina aggregates namely sillimanite, mullite and alumina rich aggregates were developed from sillimanite beach sand and calcined Al_2O_3 by reaction sintering route. The various phases present in the sintered compacts were identified by X-ray diffraction study in conjunction with infrared study. Thermal shock behaviour of the aggregates with and without Fe_2O_3 doping were measured by the room temperature flexural strength retention on ambient air quenching from 1000°C against the number of cycles. The results obtained are presented and discussed in this paper. It was found that all Fe_2O_3 containing samples show a strength enhancement on quenching by means of tempering. Attempts have been made to correlate this parameter with the microstructure and phase assembly of the product.

1. Introduction

India is one of the countries which has sufficient deposits of beach sand. Beach sand sillimanite is a by-product generated in huge quantities during the extraction of rare earth compounds. Several attempts have been made by many authors [1–5] for effective utilisation of this material. It is revealed from these studies that powdered sillimanite sand when mixed with reactive alumina in different proportions, the resultant batch after compaction and sintering at the required temperature form mullite/mullite-alumina composites. The sintered compacts in the form of aggregates have potential applications in refractory industries, as an alternative source of high alumina aggregate.

Studies on thermal shock behaviour is extremely important for refractory materials as it undergoes sudden temperature changes in most of the applications. Various workers in this field applied different methods [6–11] for thermal shock resistance determination. Although the acoustic emission method enables the moment of crack formation to be precisely detected and extensively used for examination of ceramic materials cracking under mechanical or thermal load, quenching methods are finding widespread use in practice. Peretz and Bradt [10] studied the thermal shock behaviour of high alumina refractory systems based on three different aggregates, namely andalusite, tabular alumina and calcined kaolin with regard to the effects of multiple thermal shock quench cycles on the strength degradation. The results revealed that tabular alumina aggregate based refractories retained nearly all of their strength even after seven thermal shock cycles. The strength of a ceramic material as a function of quenching temperature difference is discussed by Gebauer and Hasselman [12] on the basis of linear elastic theory. It was observed from the results of their work that to avoid catastrophic failure, specimens may be quenched from either lower or very high temperature (above the softening point of the material). Kirchner [13] summarised that the specimen quenched from temperatures at which the body is slightly plastic are more resistant to thermal shock than would normally be expected.

In this investigation, an attempt has been made to study the thermal shock behaviour of presently developed synthetic aggregates by measuring the flexural strength retention properties using the multiple thermal shock quench cycle method as adopted by Peretz and Bradt [10]. Studies have also been carried out to investigate the change in thermal shock behaviour of the aggregates doped with different proportions of Fe_2O_3 (1–4 wt%). Finally, the parameters are correlated with the microstructure and phase assembly of the sintered products.

* Corresponding author. Tel: +91-033-473-3469; fax: +91-033-473-0957.

E-mail address: tripathi@cscgcri.ren.nic.in (H.S. Tripathi).

0272-8842/99/$20.00
PII: S0272-8842(99)00010-3

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) from their Chattrapur plant in Orissa, India and calcined alumina from the Indian Aluminium Company Ltd. (INDAL), India. Chemical analysis of both the raw materials was done by conventional wet chemical method. Three batch compositions were selected for this study (Table 1) namely sillimanite composition (**S**), mullite composition (**M**) and alumina rich composition (**C**) with 57.6, 71.8 and 80.75 wt% Al_2O_3 respectively (in Al_2O_3/SiO_2 ratio). To promote the densification process, 1, 2 and 4 wt% Fe_2O_3 were used as an additive in each of these compositions.

The batch compositions as per Table 1 were attrition milled separately in aqueous medium using zirconia pot and zirconia grinding media for a optimum time period (9 h) selected from the study of the variation of specific surface area with milling time [4]. Slurry thus obtained were dried at 110 ± 5°C, sieved to break the agglomerate and subsequently pressed uniaxially into bars at about 100 MPa pressure using 5 w/v % PVA solution as binder followed by cold isostatic pressing at a pressure of 175 MPa. Green samples obtained by isostatic pressing were dried at 110 ± 5°C and fired in the temperature range of 1400–1600°C (1600°C for **S**, **M**, **C** and 1500°C for Fe_2O_3 doped samples) with 2 h soaking time in an electric furnace. The heating rate was 5°C min^{-1} upto 1100°C and thereafter 3°C min^{-1} up to the final firing temperature. Sintered products thus obtained were characterised in terms of bulk density, apparent porosity, flexural strength at room temperature (RT) and microstructural analysis by scanning electron microscopy (SEM), phase identification by XRD and infrared spectroscopy (IR).

Table 1
Batch compositions and sample codes selected for the study

Sample code	Raw materials (wt%)		
	Sillimanite sand	Calcined Al_2O_3	Fe_2O_3
Sillimanite composition			
S	100.00	NIL	NIL
SF1	99.00	NIL	1.00
SF2	98.00	NIL	2.00
SF4	96.00	NIL	4.00
Mullite composition			
M	68.97	31.03	NIL
MF1	68.28	30.72	1.00
MF2	67.59	30.41	2.00
MF4	66.21	29.79	4.00
Al_2O_3 rich composition			
C	48.29	51.71	NIL
CF1	47.80	51.20	1.00
CF2	47.32	50.68	2.00
CF4	46.35	49.65	4.00

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

Due to close similarity in the XRD pattern of sillimanite and mullite, IR study was also conducted to differentiate them. 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 pattern were recorded for the Braggs' angle (2θ) range 15–60°. IR-spectrometer was used to record IR transmission spectra using KBr disc method and IR transmission was recorded over the wave number range 400–4000 cm^{-1}.

Thermal shock resistance behaviour of the samples was studied by measuring the flexural strength retention on 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 the samples were quenched in ambient air, cooled for 10 min followed by reheating at 1000°C for 10 min. This cycle was repeated and retained flexural strength was measured at a regular interval of 2 cycles. 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 $55 \times 5 \times 5$ mm. The samples used were polished and edges were chamfered with a diamond disc. Three samples were taken to determine the retained flexural strength at each test and the average values have been reported here.

Microstructure evaluation of the sintered compacts was done by scanning electron microscopy using sputtered carbon coating on the polished surface of the sintered samples after thermal etching.

3. Results and discussion

The chemical composition of the major raw materials use in this study are given in Table 2. It indicates, that sillimanite sand contains higher silica (40.3 wt%) than that of the stoichiometric amount (~37 wt%), and this excess silica occurs in the sand as quartz and the alumina used was mostly α-Al_2O_3 in nature as envisaged by XRD study in our previous work [4]. Densification behaviour of the samples was reported earlier [2]. It was found that the magnitude of bulk density is directly proportional to the Al_2O_3 content particularly at higher sintering temperature. Without Fe_2O_3, sillimanite composition (**S**) requires 1550°C to achieve the highest density where as mullite composition (**M**) and alumina rich composition (**C**) due to their higher alumina content requires 1600°C. Fe_2O_3 favours the densification process and 2 wt% Fe_2O_3 is sufficient to bring down the

Table 2
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	—

densification temperature to 1500°C. Apparent porosity data [2] also supports the above observation.

IR patterns of samples **S**, **M** and **C** sintered at 1550°C are depicted in Fig. 1. In all the cases the absence of a characteristic sharp absorption peak at 1175 cm^{-1} clearly indicates almost complete conversion of sillimanite to mullite [14] at the present sintering temperature. XRD patterns of few Fe_2O_3 doped samples sintered at 1500°C are shown in Fig. 2. It may be revealed from Fig. 2 that all the samples contain mullite as the major crystalline phase. A small amount of corundum was also noticed in the alumina rich **CF4** sample.

In this case Fe_2O_3 promotes the densification by liquid phase sintering which is detrimental to high temperature properties. An attempt was also made to study the thermal shock behaviour of Fe_2O_3 doped samples and the results are compared with the Fe_2O_3 free samples. Since most of the Fe_2O_3 containing samples achieves their highest bulk density at 1500°C, these samples were selected to study the thermal shock behaviour and results are compared with Fe_2O_3 free samples sintered at 1600°C (**S**, **M** & **C**). Fig. 3(a)–(c) compare the flexural strength (RT) behaviour of the sintered specimens with regard to the effects of multiple thermal shock quench cycles from 1000°C to room temperature in ambient air. It may be observed from Fig. 3(a) that

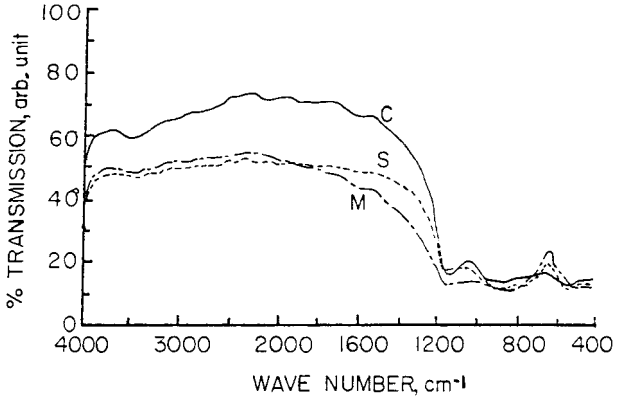

Fig. 1. IR absorption spectra of the samples **S**, **M** and **C** sintered at 1500°C showing the absence of characteristic sillimanite absorption peak at 1175 cm^{-1}.

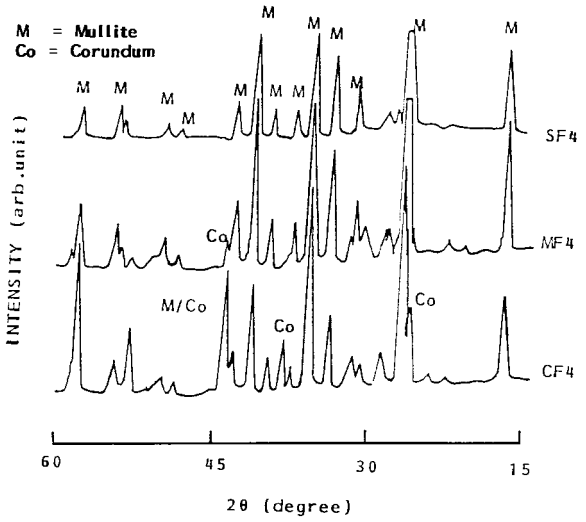

Fig. 2. XRD pattern of the samples **SF4**, **MF4** and **CF4** fired at 1500°C 2 h^{-1}.

the sample '**S**' (100% sillimanite beach sand) lost a major portion of its strength after the initial thermal shock quench cycle where as mullite sample (**M**) and alumina rich sample (**C**) [Fig. 3(b) & (c)] samples incurred no damage in terms of strength degradation upto 4 cycles. Since '**M**' & '**C**' samples contain a higher amount of mullite (low thermal expansion) and corundum (high thermal conductivity) they are more resistant to thermal shock compared to '**S**' composition. Peretz and Bradt [10] also found that calcined kaolin aggregate based refractories which are characterized by the lowest mullite and corundum contents has poorest resistance to thermal shock damage in comparison to andalusite and tabular alumina based aggregate having higher amount of mullite and corundum.

One of the interesting features observed from Fig. 3(a)–(c) is that, in the case of Fe_2O_3 containing samples there is a strength enhancement up to the 2nd cycle and in most of the cases strength degradation was started after the 4th cycle. The initial strengthening during thermal cycling may be due to the effect of tempering. A similar observation was also noticed by different investigators [15–17]. Gebauer and Hasselman [12] working on mullite ceramics observed that at higher quenching temperature difference (ΔT) strength was improved rather than degraded. Fe_2O_3 containing samples would be more amenable to being tempered due to their higher glass content and may have lower creep resistance. Sillimanite composition shows strength degradation from the very beginning of the thermal shock cycle. This suggests that sillimanite composition does not temper easily. Due to this fact, such a type of composition may have excellent creep resistance, which is under investigation. In all the cases, rate of strength degradation after 4 cycles is found to be more in the case of 4 wt% Fe_2O_3 doped samples. The gradual

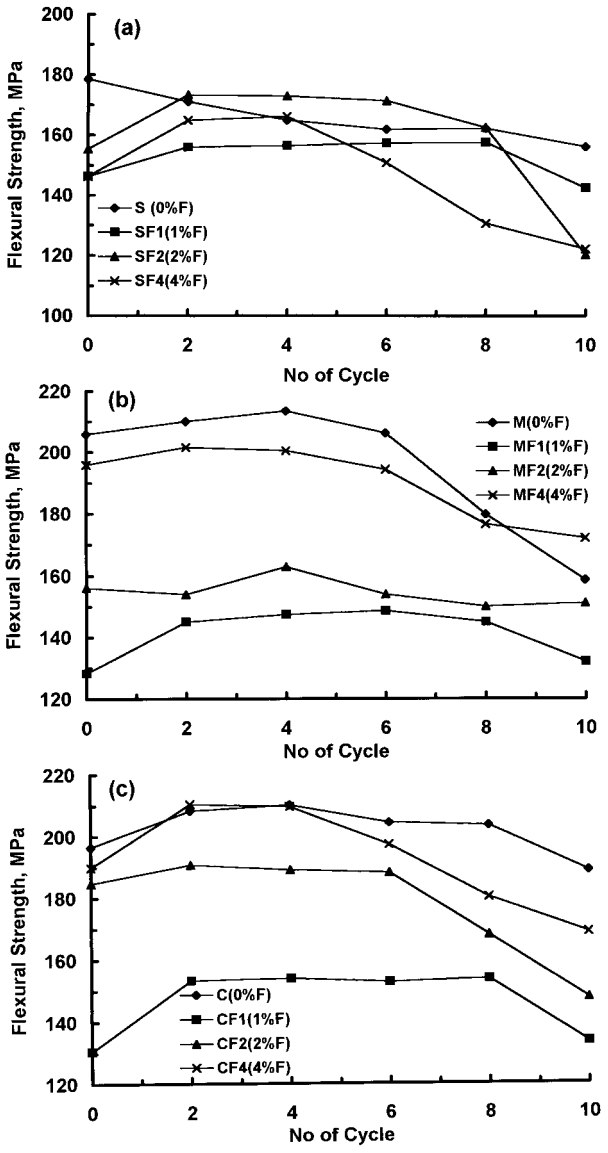

Fig. 3. Variation of flexural strength of the aggregates with the number of quench cycle. (a)- Sillimanite composition (**S**), (b)- Mullite composition (**M**) and (c)- Alumina rich composition (**C**). [Fe_2O_3 content of the samples were indicated within brackets in sample designation as %**F**].

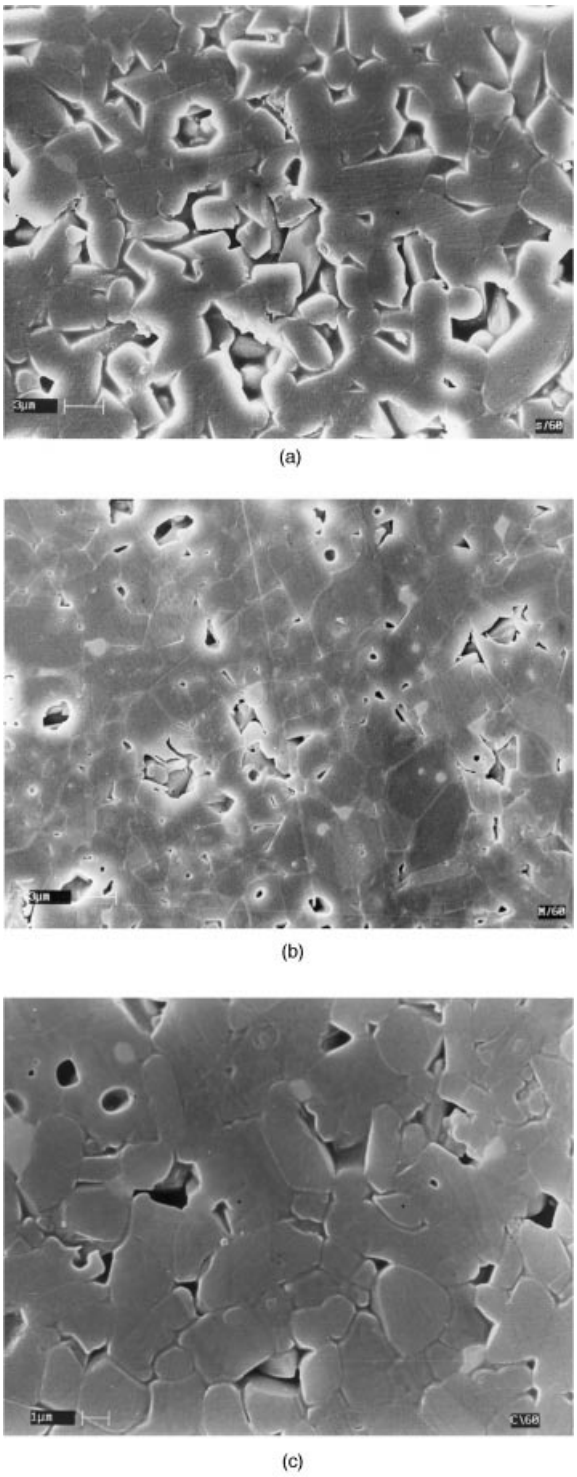

Fig. 4. Scanning electron photomicrograph of the samples fired at 1600°C 2 h^{-1}. (thermal etching) (a) - **S**, (b) - **M** and (c) - **C**.

decrease in strength after the 4th cycle could be due to the thermal fatigue by subcritical crack growth as expected at higher temperature differences of thermal shock [18,19].

Scanning electron photomicrographs of the samples sintered at 1600°C 2 h^{-1} are shown in Fig. 4. It was found that microstructure is very much dependent on the Al_2O_3/SiO_2 ratio. Needle shaped mullite formation is observed in sillimanite composition, whereas it is non-acicular in mullite and alumina rich composition. Fig. 5 depicted the scanning electron photomicrograph of the samples **MF4** and **CF2** sintered at 1500°C 2 h^{-1}. Since Fe_2O_3 increases the liquid phase formation at the present sintering temperature, Fe_2O_3 doped mullite and alumina rich samples produce needle shaped mullite. Some abnormal grain growth is observed in the **MF4** sample. Although a major part of the Fe_2O_3 enters into the mullite structure by solid solution formation, some amount of glassy phase formation is noticed in the SEM photomicrograph of Fe_2O_3 doped samples. Presence of this glassy phase might

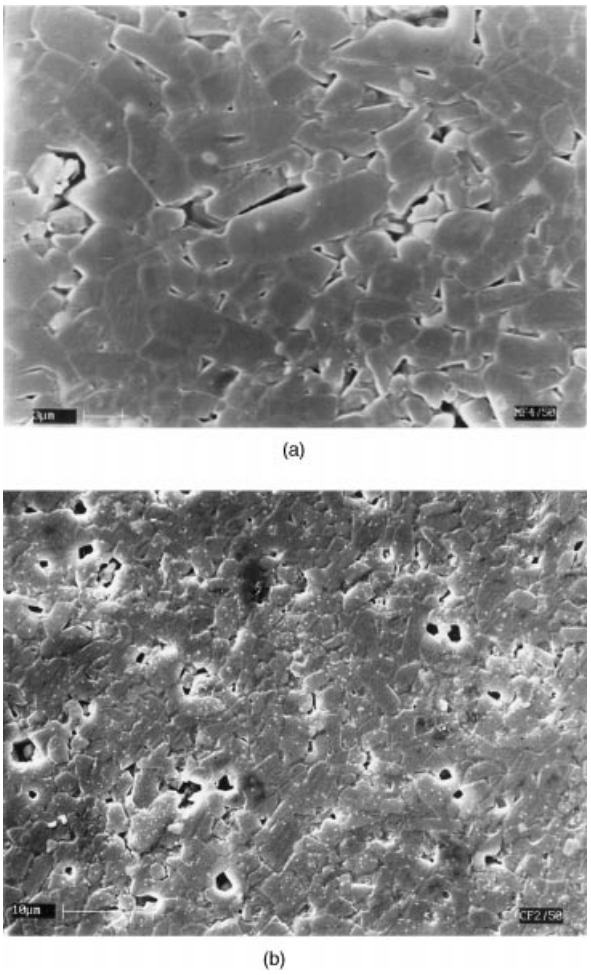

Fig. 5. Scanning electron photomicrograph of the samples fired at 1500°C 2 h^{-1}. (Thermal etching) (a) - **MF4** and (b) - **CF2**.

have been responsible for comparatively low thermal shock resistance of Fe_2O_3 doped samples.

4. Conclusions

From the present investigations, the following conclusions are drawn.

1. Sillimanite, mullite and alumina rich dense refractory aggregates have been synthesized from sillimanite beach sand and calcined Al_2O_3 through the reaction sintering route. Densification of the system and phases assembly of the sintered compacts depend on the Al_2O_3/SiO_2 ratio.
2. Fe_2O_3 doping promotes densification by liquid phase formation and favours the grain growth. Fe_2O_3 enters into the mullite structure by solid solution formation.
3. The samples containing higher amounts of mullite and corundum (**M** & **C**) are more resistant to thermal shock than to sillimanite composition.
4. Fe_2O_3 doped samples showed an initial increase in strength upto 2 cycles of thermal shock test followed by its retainment upto 4 cycles. Strength degradation was found to be started after 4 cycles and degradation rate was more in the case of 4 wt% Fe_2O_3 doped samples.
5. Microstructure of the sintered products is very much dependent on the Al_2O_3/SiO_2 ratio. Without Fe_2O_3, mullite formed in sillimanite composition is needle shaped and it is non-acicular in alumina rich composition.

Acknowledgements

The authors wish to thank Director, Central Glass & Ceramic Research Institute for his kind permission to publish this paper. Valuable suggestions and support received from Prof. N. K. Mitra, University of Calcutta, India and Dr. S. K. Das, Mr. A. Ghosh and Dr. B. Mukherjee, Scientists, CGCRI during the course of this study are gratefully acknowledged.

References

[1] S. Maity, T.K. Mukhopadhyay, B.K. Sarkar, Strength of sillimanite sand reinforced porcelain subjected to thermal shock, J. Eur. Ceram. Soc. 17 (1997) 749–752.
[2] H.S. Tripathi, Studies on mullite-alumina composites derived from sillimanite beach sand, based on the talk delivered in the Ph. D. seminar prior to submission of the thesis for the degree of D. Phil. (Tech.), Calcutta University, India, September 1997.
[3] S.K. Das, S. Kumar, P.K. Daspoddar, Effect of synthetic refractory aggregates on the hydraulic and other properties of commercial high Al_2O_3 cement. Industrial Ceramics 17(1) (1997) 17–22
[4] H.S. Tripathi, G. Banerjee, Effect of chemical composition on sintering and properties of Al_2O_3-SiO_2 system derived from sillimanite beach sand, Ceram. Int. 25 (1) (1999) 19–25.
[5] G. Banerjee, Beach sand minerals—A new material resources for glass and ceramics, Bull. Mater. Sci. 21 (4) (1999) 349–354.
[6] S.B. Tucholka, T.B. Wala, Thermal shock acoustic emission and microstructure of refractories I. High alumina refractories (60–90% Al_2O_3), Ceram. Int. 20 (1994) 359–360.
[7] G.C. Robinson, C.R. Reese, E.A.Jr. Laroche, Determination of thermally induced acoustic emissions of ceramics, Am. Ceram. Soc. Bull. 53 (6) (1974) 482–485.
[8] E. Glenny, M.G. Royston, Transient thermal stress promoted by rapid heating and cooling of brittle circular cylinders, Trans. Brit. Ceram. Soc. 57 (1958) 645–677.
[9] M. Hamidouche, N. Bouaouadja, H. Osmani, R. Torecillias, G. Fantozzi, Thermomechanical behaviour of mullite-zirconia composite, J. Eur. Ceram. Soc. 16 (1996) 441–445.
[10] I. Peretz, R.C. Bradt, Andalusite derived mullite matrix refractories, Ceram. Trans. 6 (1990) 613–633.
[11] K.T. Farber, M.D. Huang, A.G. Evans, Quantitative studies of thermal shock in ceramic based on a novel test technique, J. Am. Ceram. Soc. 64 (5) (1981) 291–301.
[12] J. Gebauer, D.P.H. Hasselman, Elastic-plastic phenomena in the strength behaviour of an aluminosilicate ceramic subjected to thermal shock, J. Am. Ceram. Soc. 55 (9) (1972) 468–469.

[13] H.P. Kirchner, Strengthening of Ceramics, Marcel Dekker, Inc. New York, 1979, pp. 31–131.
[14] A.S. Navale, N.K. Rao, S.P. Chakravarty, R. Bhat, S.K. Roy, Analysis of mineral transformation by infrared spectroscopy: Sillimanite to mullite, in: M.D. Shastry, A.G. Page (Eds.), Proc. 5th National Symp. "Analytical Spectroscopy including Hyfenated Techniques", Ind. Anal. Chemistry, 1988, pp. 115–119.
[15] J. Gebauer, D.A. Krohn, D.P.H. Hasselman, Thermal-stress fracture of a thermomechanically strengthened aluminosilicate ceramic, J. Am. Ceram. Soc. 55 (4) (1972) 198–201.
[16] H.P. Kirchner, R.E. Walker, R.M. Gruver, Strengthening alumina by quenching in various media, J. Appl. Phys. 42 (10) (1971) 3685–3692.
[17] H.P. Kirchner, R.M. Gruver, R.E. Walker, Strengthening alumina by glazing and quenching, Bull. Am. Ceram. Soc. 47 (9) (1968) 798–802.
[18] D.P.H. Hasselman, Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics, J. Am. Ceram. Soc. 52 (11) (1969) 600–604.
[19] D.P.H. Hasselman, Strength behavior of polycrystalline alumina subjected to thermal shock, J. Am. Ceram. Soc. 53 (9) (1970) 490–495.