ELSEVIER

Ceramics International 26 (2000) 347–350

CERAMICS
INTERNATIONAL

Sol–gel mullite as the self-bonding material for refractory applications

D. Amutha Rani [a,*], F.D. Gnanam [b]

[a]Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan
[b]Division of Ceramic Technology, Department of Chemical Engineering, Anna University, Chennai -600 025, India

Received 12 January 1999; received in revised form 18 January 1999; accepted 25 February 1999

Abstract

The physico-chemical properties of permanent binders used in refractories play a vital role in deciding high temperature mechanical properties. The presence of a glassy phase in the matrix of the refractory may not affect the low temperature properties significantly, however the high temperature properties are very much reduced. In the present study, the mullite precursor derived from the sol–gel route has been used as the self-bonding material to the fused mullite aggregates. The sol–gel mullite as the permanent binder yields density up to 2.48 g/cc. The room temperature flexural strength (172 kg/cm^2) and compressive strength (785 kg/cm^2) of the self-bonded fused mullite are comparable to that of the conventional clay/alumina bonded mullite products. However, superior high temperature mechanical properties such as Hot Modulus of Rupture (HMOR) (48 kg/cm^2 at 1300°C), the retention flexural strength of 116 kg/cm^2 after 10 thermal cycles of $\Delta T = 1000°C$ and Refractoriness under load (RUL) (>1800°C) were obtained for the samples of fused mullite bonded by sol–gel mullite. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sol–gel processes; C. Thermal shock resistance; D. Mullite; E. Refractories

1. Introduction

High purity mullite is one of the prime candidate materials for high temperature structural applications because of its excellent high temperature properties such as high creep resistance [1–3] and high thermal shock resistance [4]. However, the existence of glassy phase at the grain boundaries has a strong influence on its microstructure and mechanical properties [5] at elevated temperatures. In the present study, a clear comparison has been made between the characteristics of the mullite product fabricated using clay/alumina based bonding and sol–gel derived mullite self-bonding for fused mullite aggregates. The room temperature properties such as density, porosity, MOE, MOR and the high temperature mechanical properties such as HMOR, thermal spall resistance and refractoriness under load (RUL) have been carried out and the results are discussed.

2. Experimental procedure

2.1. Material preparation

A homogeneous precursor of mullite with oxide stoichiometry has been synthesized from aluminium nitrate nano hydrate and ethyl silicate in propanol medium. The details of the experimental procedure were well documented by the authors [6]. The dried gel was heat treated at 600°C for 3 h to remove nitrate and other organic residuals. The heat-treated mullite precursor was dry milled for 3 h and further wet milled for 10 h in the planetary mill at 250 rpm using alumina balls as the grinding medium. The slurry was dried and the powder was used as the self-bonding material for the fused mullite grains.

The process of development of a refractory block is shown in Fig. 1. The commercially available fused mullite grits of sizes 8/10, 10/36, 40/F and 80/F of appropriate weight percent were mixed well with suitable temporary binders and water of appropriate quantities. The sol–gel derived mullite powder of different compositions (A1, A2, A3 and A4 — Fused mullite samples with sol–gel mullite bond of different compositions)

---

* Corresponding author. Tel.: +81-52-735-5287; fax: +81-52-735-5294.
E-mail address: amutha@rocketmail.com (D. Amutha Rani).

PII: S0272-8842(99)00062-0

were added to the mixture. Similarly, the conventional bonding material (AC-mullite samples with alumina/clay bond; alumina and ball clay of as-received condition) of appropriate ratio were used to prepare the control specimens. All these compositions were made as per industry specifications (Carborundum Universal Ltd., Chennai, India). After thorough mixing, the compacts were made by uniaxial pressing using maxiburator of different sizes of $6 \times 1 \times 1$, $6 \times 1\frac{1}{2} \times 1\frac{1}{2}$ and $3 \times 3 \times 3$ in. The green compacts were floor dried for 12 h and then oven dried at 120°C for 12 h and the dried compacts were sintered at 1600°C for 6 h at an optimum heating rate.

3. Analytical procedure

The crystallite size of the sol–gel mullite precursor was found out using X-ray line broadening method. The density of the green and sintered compacts was determined using Archimedes' method. The modulus of elasticity was found out at room temperature for the sintered specimens using Elastosonic equipment (series Ex-1000Es, Nirmachal Engg. Ltd.). The room temperature modulus of rupture was measured by three-point bending test using Zwick Universal Testing Machine.

The hot modulus of rupture (HMOR) was carried out at 1300°C for the sintered specimen of size 6×1×1 in. The thermal spall resistance was determined by air quenching the sample with $\Delta T = 1000°C$ for 10 cycles. The retention MOR was determined, after the thermal cycles.

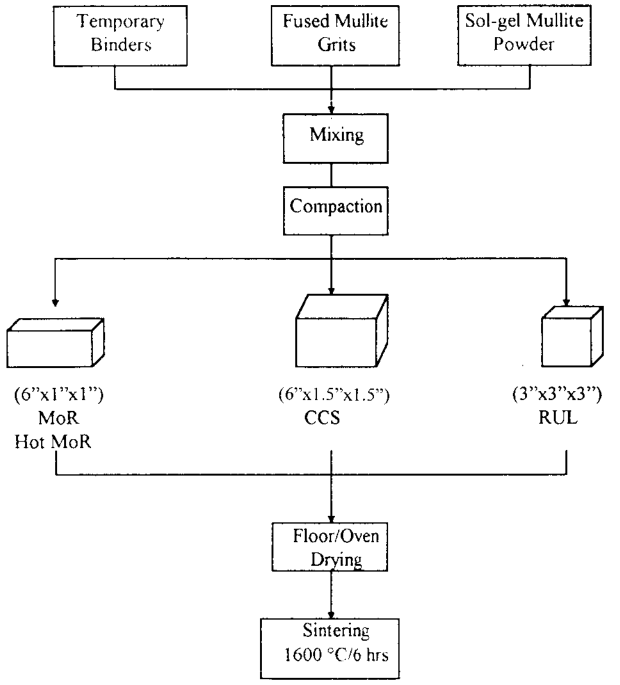

Fig. 1. Flowchart of the process development of refractory block.

Thermal expansion was measured using dialatometer from room temperature to 1550°C in air. The heating and cooling rates were maintained at 5°C/min. The refractoriness under load (RUL) test was carried out for the specimen of diameter 50 mm and height 50 mm. The load applied was 2.0 kg/cm^2.

4. Results and discussion

The mullite precursor calcined at 600°C and further wet milled for 10 h shows a higher densification than the powders calcined either at low or at high temperatures [6]. The crystallite size of the mullite powder derived from the sol–gel technique lies in the range of 20–30 nm and has been used as the self-bonding material. The green density, sintered density and the porosity of the clay/alumina bonded (control) and sol–gel mullite bonded compacts for different compositions are given in Table 1. The sintered density and the porosity of the batch A3 are similar to the values of the control specimen.

Table 2 gives the room temperature mechanical properties of clay bonded and sol–gel mullite bonded samples. The modulus of elasticity, modulus of rupture and cold compression strength of the self-bonded samples of batch A3 closely resemble those of the clay-bonded samples. The strength of the individual aggregates plays a major role in the overall refractory properties. In the case of the two-component refractory body concept, fracture may propagate either through permanent binder along the aggregate–binder interface or through the individual aggregates. Hence, the aggregates

Table 1
Green and sintered density of clay/aluminia bonded and sol–gel-bonded mullite

Properties	AC[a]	A1[b]	A2[b]	A3[b]	A4[b]
Green density (g/cc)	1.47	1.25	1.32	1.48	1.39
Sintered density (g/cc)	2.48	2.31	2.46	2.48	2.45
Apparent porosity (%)	18.7	20.2	15.2	19.3	20.9

[a] AC, mullite samples with aluminia/clay bond.

[b] A1, A2, A3, A4, mullite samples with sol–gel mullite bond of different compositions.

Table 2
Room temperature properties of clay/aluminia bonded and sol–gel-bonded mullite

Properties	AC[a]	A1[b]	A2[b]	A3[b]	A4[b]
MOE (GPa)	63	42	57	63	51
MOR (kg/cm^2)	178	124	160	172	153
CCS (kg/cm^2)	800	545	730	784	620

[a] AC, mullite samples with aluminia/clay bond.

[b] A1, A2, A3, A4, mullite samples with sol–gel mullite bond of different compositions.

Table 3
High temperature properties of clay/aluminia bonded and sol–gel-bonded mullite

Properties	AC[a]	A1[b]	A2[b]	A3[b]	A4[b]
HMOR (kg/cm^2)	36	19	31	48	29
Retained MOR (kg/cm^2)	90	65	82	116	86
RUL (°C)	1700	–	> 1800	1800	1740

[a] AC, mullite samples with aluminia/clay bond.

[b] A1, A2, A3, A4, mullite samples with sol–gel mullite bond of different compositions.

are not only the load bearing constituents, but perform a vital role as crack-arresting sites. Similarly, the permanent binder (sol–gel mullite) integrates the aggregates through chemical bonding and plays an important role as a load-bearing constituent to maintain the structural integrity during service conditions.

The high temperature mechanical properties such as HMOR, thermal spall resistance and refractoriness under load (RUL) of the conventional clay bonded and the self-bonded mullite are given in Table 3. The modulus of rupture at 1300°C for mullite product of batch A3 is 48 kg/cm^2. This value is higher than the conventional clay bonded mullite (36 kg/cm^2). These results show that the sol–gel mullite grain is sufficiently fine to develop better bonding with the fused mullite refractory grain during sintering. Application of conventional aluminosilicate castables is shrinking day by day in furnaces/vessels operating at high temperature due to inferior high temperature properties. High binder content is largely responsible for these disadvantages. To overcome the demerits of the conventional castable, a new generation of self-bonding agents can be used in order to improve the high temperature mechanical properties. Narayanan et al. [7] have replaced cement binder for hydraulic setting with alumina binder and they have identified that the HMOR (8.0 N/mm^2) was found to be superior when compared to the cement binder (5.5 N/mm^2). The thermal spall resistance at $\Delta T = 1000°C$ after 10 cycles of the sol–gel mullite bond shows higher retention value of 116 kg/cm^2 than the samples produced by clay bond (90 kg/cm^2). When sol–gel mullite powder is used as the bonding material, there is no glassy phase present in the system and hence the system becomes monophasic in nature. Such a monophasic system experiences no additional thermal stress due to the presence of secondary phases. Hence a higher retained stress is expected for a monophasic system and has been observed in the present investigation.

Fig. 2. shows the thermal expansion curve in the heating and cooling cycle. The mullite sintered body shows large thermal hysteresis between heating stage and cooling cycle. The hysteresis curve shows very low expansion during the heating stage and high expansion at high temperatures. During the heating stage, the closing of grain boundary microcracks gives very low expansion, and at high temperature, the microcracks closed completely and each grain connected together, which shows relatively higher expansion [8]. The kink points of heating curves were observed at 200°C due to decomposition of organic radicals.

The thermal expansion at various temperatures at a constant load of 2 kg/cm^2 is shown Fig. 3 for different batch compositions. Refractoriness Under Load (RUL) test performed on the sintered specimens showed that the sol–gel-bonded products have much higher values (up to 1800°C) when compared to clay-bonded samples

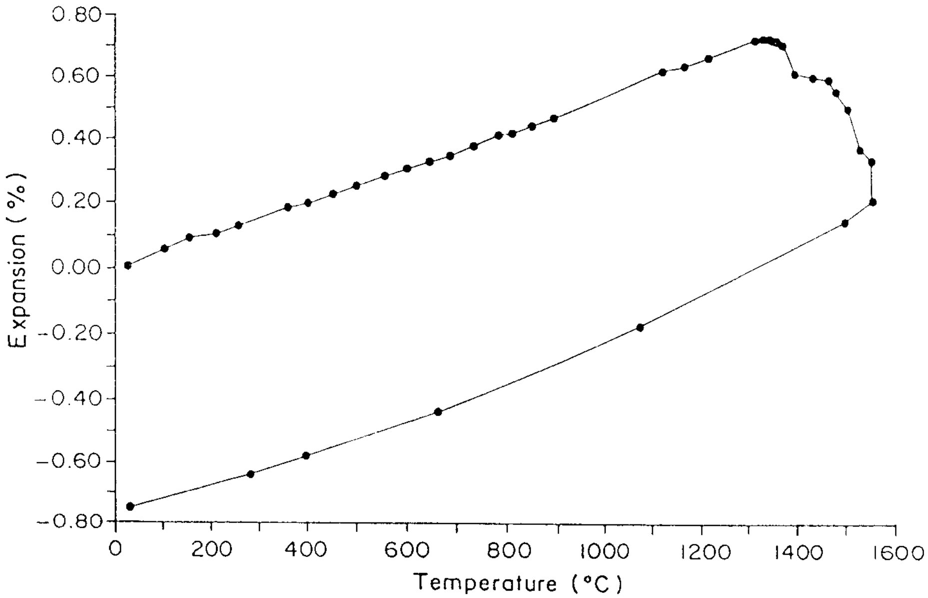

Fig. 2. Thermal expansion of heating and cooling cycle of the sol–gel derived mullite.

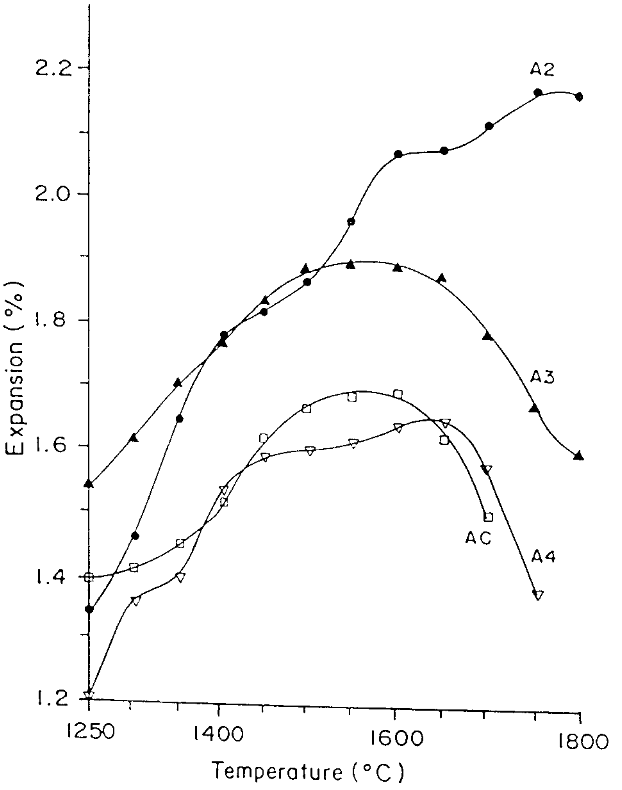

Fig. 3. Thermal expansion at various temperatures at a constant load (2.0 k/cm^2).

(1700°C). It is also interesting to note that the batch A2 has a higher value than A3. This result clearly indicates that there is no glassy phase present in the system. Since mullite is the high temperature bond with no low melting phases such as anorthite or gehlnite, the refractoriness is much higher [9]. The refractory block withstanding the temperature up to 1800°C is mainly due to the addition of phase pure mullite as the self-binder.

The increase in high temperature mechanical properties reveal that the sol–gel mullite is highly reactive due to its high surface area (> 40 m^2/g) and chemical purity than the conventional clay-bonded mullite. It may also be noted that the sol–gel mullite bond is completely free from glassy phase whereas the clay/alumina bond may have unreacted glassy phase. The presence of glassy phase retards the high temperature property considerably.

5. Conclusion

The room temperature properties of samples prepared using sol–gel derived mullite as self-bond for fused mullite aggregates are comparable to that of the clay/alumina bonded products. However, the high temperature properties like hot MOR (at 1300°C), thermal spalling resistance and RUL are much higher for sol–gel-derived mullite bonded products. These superior properties are due to the high surface area, high chemical purity and total absence of glassy phase in the bond.

Acknowledgements

The financial support from Department of Science and Technology, New Delhi, Council of Scientific and Industrial Research, New Delhi, India and Carborundum Universal Ltd., Chennai, India to carry out this study is gratefully acknowledged.

References

[1] H. Onishi, K. Maeda, T. Nakamura, T. Kawanami, High temperature mechanical properties of mullite ceramics, in: S. Somiya, et al. (Eds.), Ceramic Transactions, Mullite and Mullite Matrix Composites, The American Ceramic Society, Westerville, 1990, pp. 605–612.
[2] Y. Okamaoto, H. Fukudome, K. Hayashi, T. Nishikawa, Creep deformation of polycrystalline mullite, J. Eur. Ceram. Soc. 6 (1990) 1661–1668.
[3] H. Ohira, H. Shiga, M.G.M.U. Ismail, Z. Nakai, T. Akiba, E. Yasuda, Compressive creep of mullite ceramics, J. Mater. Sci. Lett. 10 (1991) 847–849.
[4] I. Peretz, R.C. Bradt, Andalusite-derived mullite matrix refractories, in: S. Somiya, et al. (Eds.), Ceramic Transactions, Mullite and Mullite Matrix Composites, The American Ceramic Society, Westerville, 1990, pp. 613–633.
[5] H. Ohira, M.G.M.U. Ismail, Y. Yamamoto, T. Akiba, S. Somiya, Mechanical properties of high purity mullite at elevated temperatures, J. Eur. Ceram. Soc. 16 (1996) 225–230.
[6] D. Amutha Rani, F.D. Gnanam, Mater. Sci. Eng. A264 (1999) 254–261.
[7] S. Narayanan, P.P. Vajifdar, D.G. Banawalikar, S.D. Majumdar. Development of new generation easy to use castable, in: 2nd IREFCON Proc., vol. 1, 1996, pp. 82–90.
[8] T. Yano, M. Kiyohara, N. Otsuka, Thermal and mechanical properties of aluminium titanate–mullite composites — 3, J. Ceram. Soc. Japan 100 (1994) 482–487.
[9] Subatra B. Recent trends in monolithic refractories, in: 2nd IREFCON, Proc., vol. 1, 1996, pp. 19–33.