Role of Cr_2O_3 on the mullittization of di-phasic Al_2O_3-SiO_2 gel

(Efeito do Cr_2O_3 na mulitização do gel difásico Al_2O_3-SiO_2)

Jagannath Roy[1], Narayan Bandyopadhyay[2], Santanu Das[3], Saikat Maitra[4]
[1]Camellia Institute of Technology, Badu, Madhyagram, Kokata-700129, India
[2]Govt. College of Engineering and Ceramic Technology, 73, A.C. Banerjee Lane, Kolkata-700010, India
[3]Mechanical and Metallurgical Engineering, Florida International University, USA
[4]Universiti Teknologi PETRONAS, Tronoh-31750, Perak, Malaysia
maitrasaikat@rediffmail.com

Abstract

Diphasic Al_2O_3-SiO_2 gel was synthesized by sol-gel route from inorganic salts following aqueous phase colloidal interaction and the effect of Cr_2O_3 additive on the formation of mullite ceramics from this diphasic gel was investigated. The gel powder was thoroughly characterized by chemical analysis, measurement of surface area, bulk density and FTIR spectroscopy. The calcined gel was compacted with Cr_2O_3 additives in three different proportions (ca. 1, 2 and 3 wt%) and heat treated at different elevated temperatures (ca, 1400, 1500 and 1600 °C). The analyses of microstructure and phase composition of the sintered masses were carried out by scanning electron microscopy and XRD technique. The morphology of the mullite crystals changed significantly in the presence of the additives. It has been observed that more than 7% more mullite has been formed with the addition of maximum 3% additive only. Using the additive, the maximum reduction in apparent porosity was about 30% and maximum improvement in density in the sintered compacts was about 14%. The flexural strength and fracture toughness of the sintered compacts also improved by 16% and 6% respectively in the presence of the Cr_2O_3 additive under the experimental condition.

Keywords: mullite, diphasic gel, Cr_2O_3, additive.

Resumo

Géis bifásicos de Al_2O_3-SiO_2 foram sintetizados pela rota sol-gel de sais inorgânicos seguindo interação coloidal de fase aquosa sendo investigado o efeito da adição de Cr_2O_3 na formação de cerâmicas de mulita a partir deste gel bifásico. O pó do gel foi totalmente caracterizado por meio de análise química, medida de área de superfície específica, densidade e espectroscopia na região do infravermelho por transformada de Fourier. O gel calcinado foi compactado com adições de Cr_2O_3 em três diferentes proporções (~ 1, 2 e 3 peso%) e tratado termicamente a diferentes temperaturas (~ 1400, 1500 e 1600 °C). As análises de microestrutura e de composição de fases das massas sinterizadas foram feitas por microscopia eletrônica de varredura e difração de raios X. A morfologia dos cristais de mulita mudaram significativamente na presença de aditivos. Foi observado que mais que 7% de mulita foi formada com a adição de no máximo somente 3% de aditivo. Usando o aditivo, a redução máxima da porosidade aparente foi 30% e a máxima melhoria na densidade dos compactos sinterizados foi 14%. A resistência à flexão e a tenacidade à fratura dos compactos sinterizados também melhorou em 16% e 6% respectivamente na presença do aditivo Cr_2O_3 nas condições experimentais adotadas.

***Palavras-chave**: mulita, gel bifásico, Cr_2O_3, aditivo.*

INTRODUCTION

Several remarkable physico-chemical properties like, low thermal expansion and thermal conductivity, good thermal and chemical stability, high melting point, low creep rate, reasonable toughness and strength, thermal shock resistance, infrared transparency etc has made mullite a remarkably important engineering material [1-4]. Therefore mullite are widely used in the production of heat resistant materials in heat insulation, corrosion resistant ceramics, high performance composites, computer chips etc. [5, 6]. Mullite is basically a non-stoichiometric compound and its molecular formula can be represented as $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$ where x denotes the number of missing oxygen and atoms per unit cell, varying between 0.17 and 0.59 [7]. Recently chemically synthesized precursors have been widely employed for the synthesis of mullite where the precursors are converted to mullite in a low temperature range from ~ 850 to ~ 1350 °C [8-10]. Mullite synthesized by this method is known as 'chemical mullite' [11]. The importance of these preparation methods has increased within the last few years. By sol-gel process generally three sequences for mullite crystallization may be observed [12]: (i) mullite may be crystallized from the amorphous phase directly for single phase gel, (ii) mullite can be crystallized via spinel phase, and (iii) mullite also can be crystallized from the reaction of discrete crystalline or semicrystalline alumina and amorphous silica from diphasic gels. Diphasic gels as type–II precursors [13] consist of pseudo boehmite and amorphous silica at room temperature. During heat treatment boehmite forms δ-Al_2O_3, this reacts with amorphous silica to form mullite above 1250 °C. Type-III diphasic gel are non-crystalline up to 980 °C and mullite formation is preceded by the formation of a weak crystalline transient alumina such as cubic Al-Si spinel or γ-Al_2O_3 at 980 °C, which later reacts with amorphous silica to form mullite at < 1250 °C.

Mullite structure can take up considerable amount of impurities. Schneider *et al* [14] did an extensive study of the solubility of transition metal cations in mullite. It has been shown that a wide variety of transition metal s can enter into mullite structure. The solubility limit of the transition metals ions in mullite depends on their radii and the oxidation state [15].

Doping of mullite with chromium is of special interest because the low thermal expansion of mullite can be further reduced by chromium incorporation [4, 16]. The site assignment of Cr^{3+} in mullite is still questionable. Cr^{3+} cation is expected to substitute Al^{3+} in AlO_6 octahedra. However spectroscopic analyses suggested that Cr^{3+} cation could also be distributed on distorted octahedral interstitial positions outside of AlO_6 octahedra [17, 18]. Rossouw and Miller [19] studied the X-ray emission spectra of Cr_2O_3 doped mullite and came to the conclusion that Cr^{3+} was most probably located in the octahedral interstitial sites at (0, 0.25, 0). Rager *et al* [20] found that chromium incorporation in regular octahedral positions in the AlO_6 chains is preferred at a low Cr_2O_3 content, whereas incorporation in interstitial lattice sites becomes more important at higher Cr_2O_3 content. While the incorporation Cr^{3+} in AlO_6 octahedra is unambiguous, the possible interstitial sites could be in the relatively wide channels running along the c-axis, or sites close to the O_c oxygen vacancies. Fischer and Schneider [21] concluded that the small fraction of chromium cations in interstitial sites is beyond the resolution of the Rietveld refinement. Villar *et al* [22] observed that beyond a certain amount Cr_2O_3 becomes insoluble in mullite lattice and reacted with Al_2O_3 to be segregated as the second phase $(Al,Cr)_2O_3$.

In the present investigation effect of Cr_2O_3 up to 3wt.% on the formation and densification of mullite from Al_2O_3-SiO_2 diphasic gel precursor powder has been studied by analyzing the microstructure and mechanical properties of sintered products. The gel precursor was synthesized from the inorganic salts of aluminium and silicon.

EXPERIMENTAL

The aluminiumsilicate hydrogel was synthesized from the starting materials $Al(NO_3)_3.9H_2O$ and liquid sodium silicate (sp. Gr. 1.6 and molar ratio of Na_2O: SiO_2 =1:3). Both the chemicals used were of analar grade and their chemical composition is given in Table I.

Table I - Chemical constituents of the ingredients.
[Tabela I - Constituintes químicos dos ingredientes.]

Ingredients	SiO_2	Al_2O	Na_2O
Sodium silicate	29.75	-	17.41
Aluminium nitrate	-	12.98	-
Batch composition	27	73	-

Silicic acid was prepared by ion exchange process from sodium silicate using Dowex-50 cation exchanging resin in a column exchanger. 7% (w/v) sodium silicate solution was used as the feed with a flow rate of 200 mL/min. Silica sol was prepared by ultrasonic dispersion of the generated silicic acid (5%w/v) in aqueous phase. Silica sol was mixed with 10% (w/v) $Al(NO_3)_3.9H_2O$ solution stoichiometrically to attain a molar ratio of 3:2 for Al_2O_3 and SiO_2 in the mix. The pH of the solution was 2. To the mixed solution 1:1 ammonia solution was added slowly with stirring till a neutral pH was attained. The mixed sol was allowed to age to form the gel. The gel was filtered, washed thoroughly, dried at 80 °C, followed by calcination at 800 °C for 2 h. The calcined gel was properly pulverized in a pot mill and was characterized by chemical analysis, measurement of surface area and bulk density. The results are given in Table II.

Table II - Physicochemical properties of the hydrogel.
[Tabela II - Propriedades físico-químicas do hidrogel.]

Composition	Properties
SiO_2	17.86
Al_2O_3	48.23
Ignition Loss	33.91
Bulk density (g/cm^3)	0.27
Sp. Surface area (m^2/g)	170

The calcined gel was thoroughly ground with Cr_2O_3 (reagent grade) additive in different ratios in a pot mill to ensure proper homogeneity in the mixes. The composition of the different batches is given in Table III.

Table III - Batch composition of the samples.
[Tabela III - Composição dos 4 tipos de amostras.]

Batch n.	Al_2O_3-SiO_2 Hydrogel	MnO_2
1	100	0
2	99	1
3	98	2
4	97	3

The powder mixes were compacted at 100 MPa. The samples were fired in an electrically heated muffle furnace at three different final temperatures, ca. 1400, 1500 and 1600 °C, with 2 h of soaking period in each case. Bulk density and apparent porosity of the sintered samples were measured following the procedures described in BS 1902, Part 1A, 1966. The flexural strength of the sintered samples were determined from a three point bending strength with a span of 30 mm and a loading rate of 0.5 mm/min. Fracture toughness was determined by using an indentation micro-crack method with a load of 5 kg. XRD pattern of the samples was taken with a Rigaku X-ray diffractometer with Cu target (Miniflex, Japan). Scanning electron microscopy investigation of the samples was carried with FEI Quanta microscope (US).

RESULTS AND DISCUSSION

Silica sol synthesized from sodium silicate by ion exchange process was a appositively charged colloid and after generation it did not show any tendency of polymerization. When silica sol was added to $Al(NO_3)_3$ solution, the solution became acidic. With the addition of ammonium hydroxide aluminum hydroxide and polysilicic acid gels were formed separately resulting in the formation of di-phasic aluminosilicate gel. In this system discrete aluminum hydroxide gel particles was likely to be distributed uniformly in the high molecular weight polysilicic acid gel network.

The precursor powder is expected to have considerable surface activity as it had a very low bulk density (0.27 g/cm^3) and a considerably high surface area (70 m^2/gm). As the hydro-gel contained significant amount of water (33.91%) it was calcined at 800 ^{o}C to prevent excessive shrinkage during sintering. The composition of the aluminosilicate was intentionally kept slightly in the alumina rich zone of the mullite to minimize the formation of glassy phase after sintering. After synthesis no deviation was observed from the parent batch composition in the synthesized material.

In the FT-IR spectra of the sample (Fig. 1) the peaks at 3464 cm^{-1} and 1637 cm^{-1} were assigned to the stretching and bending mode of adsorbed water since the precursor gel was prepared under basic condition where the gelation occurred rapidly. The $Al(OH)_3$ was precipitated out in colloidal form along with precipitates of $Si(OH)_4$ and they grew rapidly eliminating the possibility of forming an aluminosilicate precursor [23]. The band at 3151 cm^{-1} was assigned to the OH^- stretching mode of these hydroxides. Corresponding OH^- bending vibration was observed at 1105.7 cm^{-1}, which overlapped with the stretching vibration of Si-O-Si of the gel network. The sharp peak at 1388.4 cm^{-1} indicated the presence of trace amount of nitrate from the starting material aluminium nitrate in the gel structure [24]. The stretching modes of Al-O-Al linkages were observed at 618.7 and 747.7 cm^{-1}. The band at 477.9 cm^{-1} was assigned to Si-O stretching vibration. No characteristic band for Si-O-Al linkage was observed, which suggested that the precursor maintained true diphasic gel characteristics.

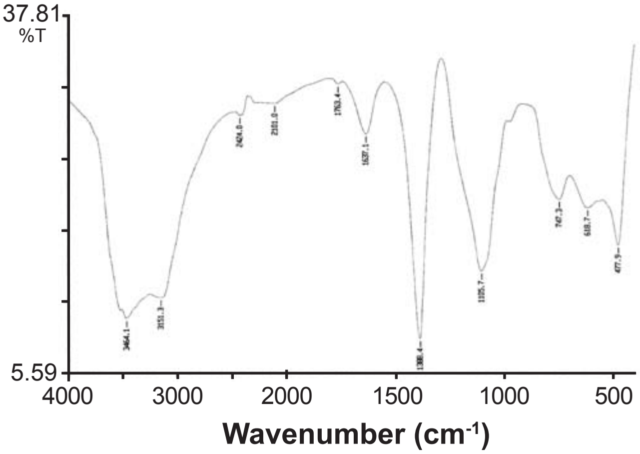

Figure 1: FT-IR spectrum of the gel sample.
[Figura 1: Espectro FTIR da amostra gel.]

Mullite formation in diphasic aluminosilicate gel is controlled by dissolution-precipitation reactions, where Al_2O_3 species dissolve in the co-existing SiO_2 liquid until a critical Al_2O_3 concentration is reached [25, 26]. Al_2O_3 particles act as the nucleus for mullite formation and higher Al_2O_3 concentrations can induce random mullite nucleation in the bulk of the SiO_2-rich phase. Therefore, the dissolution velocity of Al_2O_3 into the SiO_2 liquid is the rate limiting step for the nucleation and subsequently growth of mullite crystals.

Cr_2O_3 as an additive affected the sintering process of the calcined alumino-silicate gel. The ionic radii of Al^{3+} and Cr^{3+} are 53.5 pm and 75.5 pm, respectively [27]. As Cr^{3+} is expected to substitute Al^{3+} in AlO_6 octahedra, an expansion in the octahedral site is favoured. From the XRD diagram of

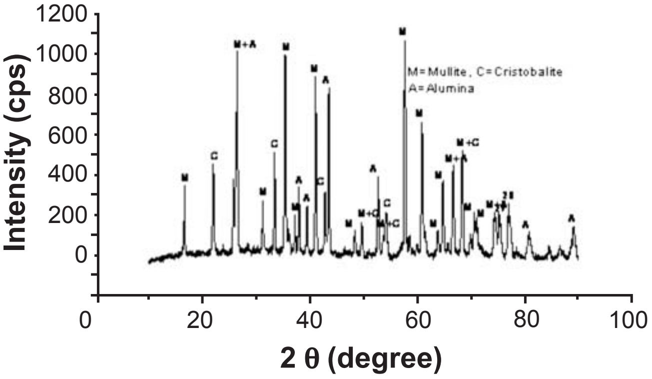

Figure 2A: X-ray diffraction pattern of the gel (no additive) sintered at 1500 ^{o}C.
[Figura 2A: Difratograma de raios X do gel sem aditivo sinterizado a 1500 ºC.]

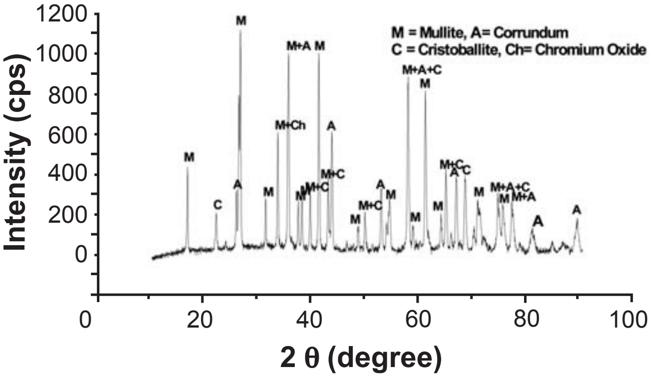

Figure 2B : X-ray diffraction pattern of the the sintered gel with 3% Cr_2O_3 at 1500 ^{o}C.
[Figura 2B: Difratograma de raios X do gel sinterizado a 1500 ºC.]

the sintered samples (Figs. 2A and 2B) it was observed with 3% Cr_2O_3 additive at 1500 ^{o}C mullite formation favoured. The calculated values of lattice parameters of un-doped mullite was like the following, a= 7.524 A^o, b= 7.672A^o and c= 2.863A^o, whereas for the sample with 3% Cr_2O_3 lattice parameter was like the following, a = 7.528A^o, b = 7.687A^o and c = 2.865A^o. It clearly indicates that as a result of Cr^{3+} substitution 1.05 % expansion in the lattice took place. From the relative intensity of the peaks it is apparent that with the addition of 3% Cr_2O_3 about 7% more mullitization can be achieved at a sintering temperature of 1500 ^{o}C.

From the SEM micrographs of the sintered samples (Figs. 3A and 3B) it is apparent that un-doped sol-gel mullite formed very small crystallites. The incorporation of titanium ions in the sol-gel mullite induced tabular crystal growth parallel to the crystallographic c-axis. With the increase in the additive growth the crystallite size increased. The average crystallite size was also calculated using Debye-Scherrer formula [28] as follows:

$D = 0.9\ \lambda\ /\ (\beta \cos \theta)$, where D is the diameter of the crystallites forming the film, λ is the wavelength of Cu-kα line, β is FWHM in radian, and θ is the Bragg angle.

$$\beta = \sqrt{\beta_0^2 - b^2}$$

where β_o is the FWHM in radians for the sample and b the FWHM in radians for the pure crystal.

The average crystallite size as calculated using Scherrer equation for sample with 3% Cr_2O_3 was 2.75 μm at 1400 ^{o}C, 2.70 μm at 1500 ^{o}C and 1.93 μm at 1600 ^{o}C. The microstructure became more cohesive with the increase in the additive content.

The variation in bulk density and apparent porosity of the samples with sintering temperature are shown in Figs. 4 and 5.

From the figures it is clear that Cr_2O_3 exhibited a positive effect on the densification of the mullite ceramics. After 1500 ^{o}C the improvement in density and reduction in apparent porosity was not significant. With 3% Cr_2O_3 content the bulk density improved by 14% and apparent porosity was reduced by 30% at a sintering temperature of 1600 ^{o}C.

The flexural strength and fracture toughness (Figs. 6 and 7) of the samples also increased in the presence of Cr_2O_3 additive. The effect was more pronounced for the batch containing 2% additive at the highest sintering temperature under investigation. A slight drop in flexural strength at the highest sintering temperature with 3% Cr_2O_3 content might be related to the formation of more glassy

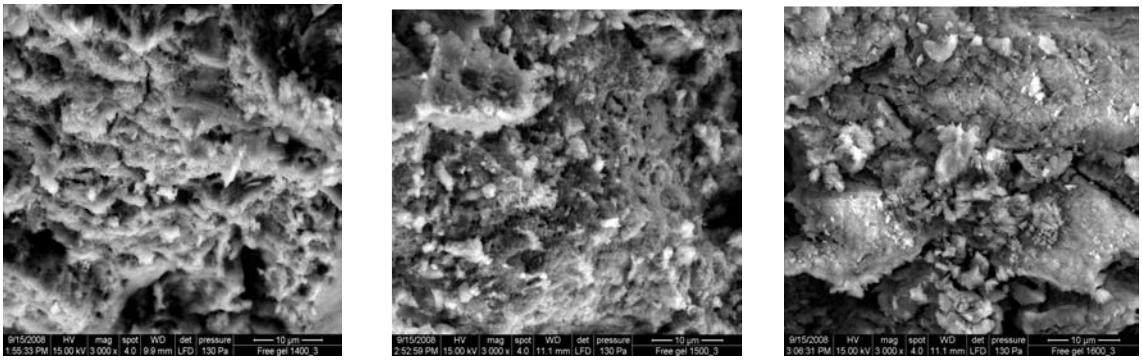

Figure 3A: Scanning electron microscopy micrograph of the sintered gel samples (no additive) (i): sintered at 1400 ^{o}C (ii) sintered at 1500 ^{o}C (iii) sintered at 1600 ^{o}C.

[Figura 3A: Micrografia obtida por microscopia eletrônica de varredura de amostras do gel sinterizado (sem aditivo) (i): sinterizado a 1400 ^{o}C (ii) sinterizado a 1500 ^{o}C (iii) sinterizado a 1600 ^{o}C.]

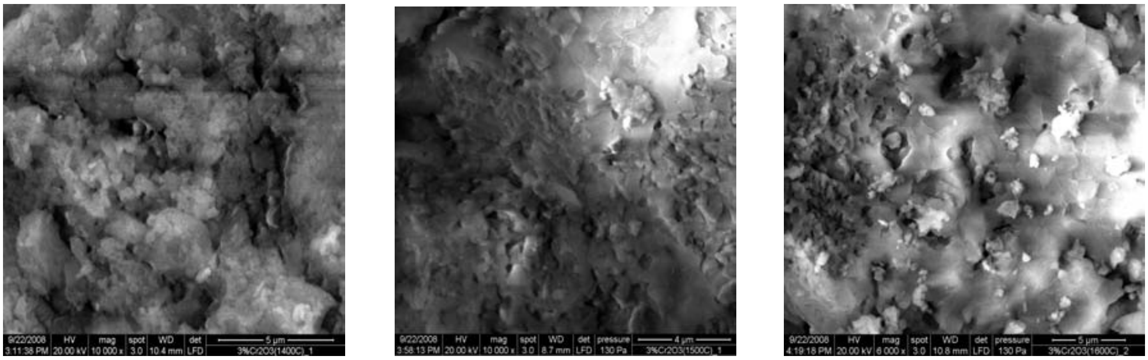

Figure 3B: Scanning electron microscopy micrograph of the sintered gel samples with 3% Cr_2O_3 additive(i): sintered at 1400 ^{o}C (ii) sintered at 1500 ^{o}C (iii) sintered at 1600 ^{o}C.

[Figura 3B: Micrografia obtida por microscopia eletrônica de varredura de amostras sinterizadas do gel com 3% do aditivo Cr_2O_3 sinterizado a 1400 ^{o}C (ii) sinterizado a 1500 ^{o}C (iii) sinterizado a 1600 ^{o}C.]

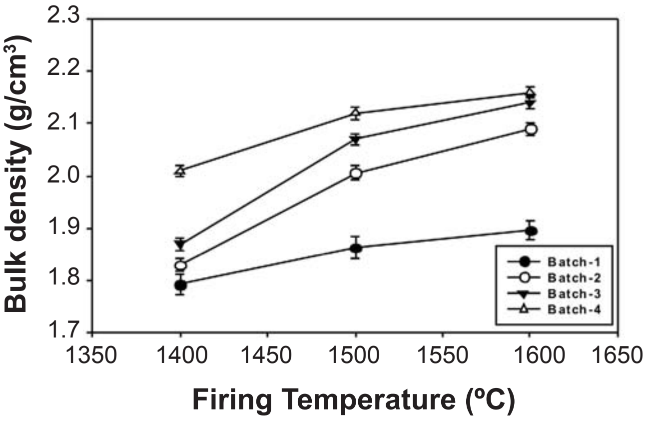

Figure 4: Variation in bulk density with firing temperature.
[Figura 4: Densidade em função da temperatura de sinterização.]

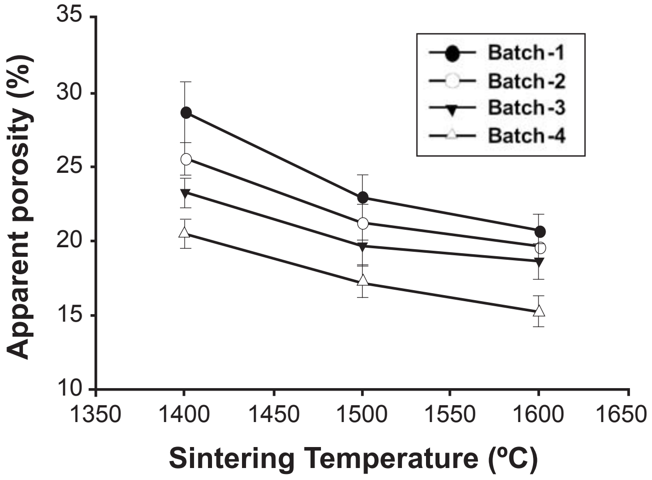

Figure 5: Apparent porosity as a function of the firing temperature.
[Figura 5: Porosidade aparente em função da temperatura de queima.]

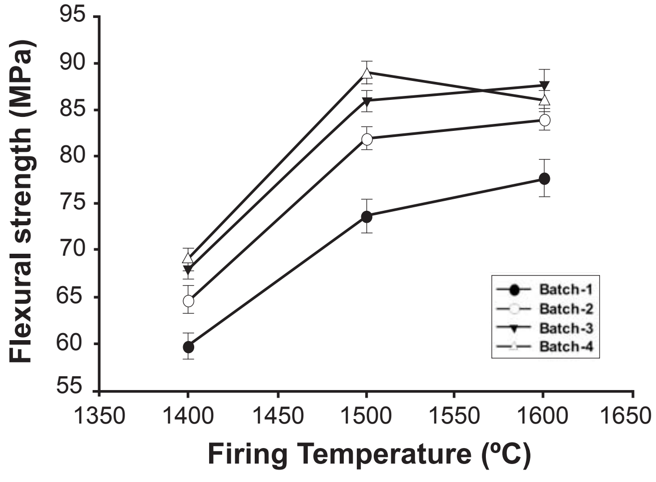

Figure 6: Variation in flexural strength with firing temperature.
[Figura 6: Variação da resistência a flexão com a temperatura de queima.]

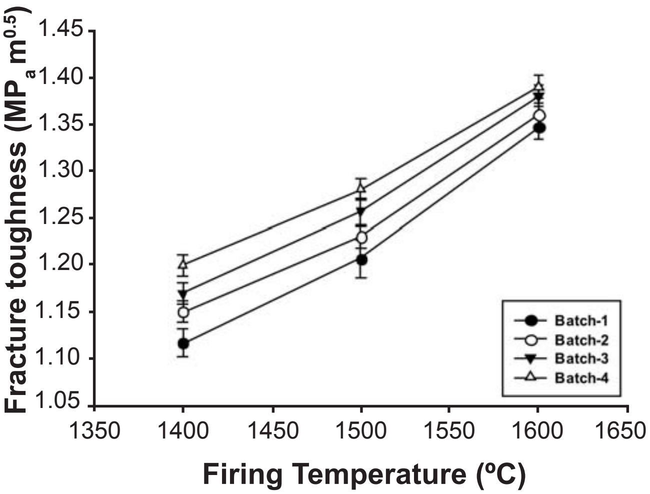

Figure 7: Variation in fracture toughness with firing temperature.
[Figura 7: Variação da tenacidade à fratura com a temperatura de queima.]

phases in the microstructure. About 16% improvement in the flexural strength of the sintered compact was obtained with 2% additive at a sintering temperature of 1600 ºC. Presence of second phase at the grain boundary comprising of Al_2O_3-Cr_2O_3 solid solution could absorb the stress by grain boundary sliding [22]. Formation of more interlocked crystalline phases in the presence of Cr_2O_3 additives can be another reason for the improvement of the mechanical strength. A small amount of highly viscous silica or aluminosilicate glass can exist at the grain boundaries, which would minimize the contribution of grain boundary sliding to the fracture stress. About 6% improvement in the fracture toughness of the sintered compact was observed with 3% Cr_2O_3 additive at a sintering temperature of 1600 ºC.

SUMMARY AND CONCLUSION

Diphasic aluminosilicate gels synthesized by the colloidal interaction of silicic acid and $Al(NO_3)_3$ solution as a precursor of mullite ceramics. The gel powder possessed very low density and high surface area and consisted of separate non-linked units of alumina and silica gel. Cr_2O_3 was used as sintering additive for the processing of mullite ceramics in different proportions. The sintering behaviour of mullite was modified by the expansion of AlO_6 sub-lattice of mullite by Cr_2O_3. The crystallite size of mullite was also modified by Cr_2O_3. Up to 1500 ºC of firing temperature the improvement in mechanical properties was observed to be significant.

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