Role of $\text{Cr}_2\text{O}_3$ on the mullitization of di-phasic $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ gel

(Efeito do $\text{Cr}_2\text{O}_3$ na mullitização do gel difásico $\text{Al}_2\text{O}_3$-$\text{SiO}_2$)

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Abstract

Diphasic $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ gel was synthesized by sol-gel route from inorganic salts following aqueous phase colloidal interaction and the effect of $\text{Cr}_2\text{O}_3$ 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 $\text{Cr}_2\text{O}_3$ 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 $\text{Cr}_2\text{O}_3$ additive under the experimental condition.

Keywords: mullite, diphasic gel, $\text{Cr}_2\text{O}_3$, additive.

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 $\text{Al}_x[\text{Al}_{2-2x}\text{Si}_{2-2x}]\text{O}_{10+x}$, 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 α-AlO$_3$, 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$_2$O$_3$ at 980 °C, which later reacts with amorphous silica to form mullite below 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$_2$O$_3$ 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$_2$O$_3$ content, whereas incorporation in interstitial lattice sites becomes more important at higher Cr$_2$O$_3$ 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$_2$ 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$_2$O$_3$ becomes insoluble in mullite lattice and reacted with Al$_2$O$_3$ to be segregated as the second phase (Al,$Cr$)$_2$O$_3$.

In the present investigation effect of Cr$_2$O$_3$ up to 3 wt.% on the formation and densification of mullite from Al$_2$O$_3$-SiO$_2$ diphasic gel precursor powder was studied by analyzing the microstructure and mechanical properties of sintered products. The gel precursor was synthesized from inorganic salts of aluminium and silicon.

**EXPERIMENTAL**

The aluminiumsilicate hydrogel was synthesized from the starting materials Al(NO$_3$)$_3$$\cdot$9H$_2$O and liquid sodium silicate (sp. Gr. 1.6 and molar ratio of Na$_2$O: SiO$_2$ =1:3). Both the chemicals used were of analar grade and their chemical composition is given in Table I.

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$$\cdot$9H$_2$O solution stoichiometrically to attain a molar ratio of 3:2 for Al$_2$O$_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>
<thead>
<tr>
<th>Ingredients</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Na$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium silicate</td>
<td>29.75</td>
<td>-</td>
<td>17.41</td>
</tr>
<tr>
<td>Aluminium nitrate</td>
<td>-</td>
<td>12.98</td>
<td>-</td>
</tr>
<tr>
<td>Batch composition</td>
<td>27</td>
<td>73</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch n.</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>Hydrogel</th>
<th>MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>99</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>98</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>97</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

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 positively charged colloid and after generation it did not show any tendency of polymerization. When silica sol was added to Al(NO₃)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/cm³) and a considerably high surface area (70 m²/gm). As the hydro-gel contained significant amount of water (33.91%) it was calcined at 800 °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 aluminum 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.

Mullite formation in diphasic aluminosilicate gel is controlled by dissolution-precipitation reactions, where Al₂O₃ species dissolve in the co-existing SiO₂ liquid until a critical Al₂O₃ concentration is reached [25, 26]. Al₂O₃ particles act as the nucleus for mullite formation and higher Al₂O₃ concentrations can induce random mullite nucleation in the bulk of the SiO₂-rich phase. Therefore, the dissolution velocity of Al₂O₃ into the SiO₂ liquid is the rate limiting step for the nucleation and subsequently growth of mullite crystals.

Cr₂O₃ as an additive affected the sintering process of the calcined alumino-silicate gel. The ionic radii of Al³⁺ and Cr³⁺ are 53.5 pm and 75.5 pm, respectively [27]. As Cr³⁺ is expected to substitute Al³⁺ in AlO₆ octahedra, an expansion in the octahedral site is favoured. From the XRD diagram of

![Figure 1: FT-IR spectrum of the gel sample.](image1)

![Figure 2A: X-ray diffraction pattern of the gel (no additive) sintered at 1500 °C.](image2A)

![Figure 2B: X-ray diffraction pattern of the gel with 3% Cr₂O₃ at 1500 °C.](image2B)
the sintered samples (Figs. 2A and 2B) it was observed with 3% Cr₂O₃ additive at 1500 °C mullite formation favoured. The calculated values of lattice parameters of un-doped mullite was like the following, a= 7.524 Å, b = 7.672Å and c= 2.863Å, whereas for the sample with 3% Cr₂O₃ lattice parameter was like the following, a = 7.528Å, b = 7.687Å and c = 2.865Å. It clearly indicates that as a result of Cr³⁺ 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% Cr₂O₃ about 7% more mullitization can be achieved at a sintering temperature of 1500 °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:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( D \) is the diameter of the crystallites forming the film, \( \lambda \) is the wavelength of Cu-kα line, \( \beta \) is FWHM in radian, and \( \theta \) is the Bragg angle.

The average crystallite size as calculated using Scherrer equation for sample with 3% Cr₂O₃ was 2.75 μm at 1400 °C, 2.70 μm at 1500 °C and 1.93 μm at 1600 °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 Cr₂O₃ exhibited a positive effect on the densification of the mullite ceramics. After 1500 °C the improvement in density and reduction in apparent porosity was not significant. With 3% Cr₂O₃ content the bulk density improved by 14% and apparent porosity was reduced by 30% at a sintering temperature of 1600 °C.

The flexural strength and fracture toughness (Figs. 6 and 7) of the samples also increased in the presence of Cr₂O₃ 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% Cr₂O₃ content might be related to the formation of more glassy
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 °C. Presence of second phase at the grain boundary comprising of Al₂O₃-Cr₂O₃ solid solution could absorb the stress by grain boundary sliding [22]. Formation of more interlocked crystalline phases in the presence of Cr₂O₃ additives can be another reason for the improvement of the mechanical strength. A small amount of highly viscous silica or alumino-silicate 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% Cr₂O₃ additive at a sintering temperature of 1600 °C.

**SUMMARY AND CONCLUSION**

Diphasic aluminosilicate gels synthesized by the colloidal interaction of silicic acid and Al(NO₃)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. Cr₂O₃ 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 AlO₆ sub-lattice of mullite by Cr₂O₃. The crystallite size of mullite was also modified by Cr₂O₃. Up to 1500 °C of firing temperature the improvement in mechanical properties was observed to be significant.

**REFERENCES**