Effect of CoO on the Formation of Mullite Ceramics from Diphasic Al$_2$O$_3$-SiO$_2$ Gel

J. Roy$^1$, N. Bandyopadhyay$^2$, S. Das$^3$ and S. Maitra*$^4$

$^1$Camellia Institute of Technology, Badu, Madhyamgram, Kolkata-700127, 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.

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Abstract

In this work the effect of CoO additive on the formation of mullite from Al$_2$O$_3$-SiO$_2$ diphasic gel has been studied. The diphasic gel precursor for mullite was synthesized by sol-gel route following aqueous phase colloidal interaction of aluminium hydroxide and silicic acid. The precursor gel powder was thoroughly characterized by chemical analysis, measurement of surface area, bulk density and also by FTIR spectroscopic studies. The gel powder was compacted with the CoO additives in different ratios and sintered at three different elevated temperatures. Microstructure of the sintered compacts was analyzed from SEM studies and phase analyses were carried out from XRD studies. It has been observed that the morphology of the mullite crystals changed significantly in the presence of the additives. As a result of the inclusion of additive maximum expansion in the b-axis of the mullite crystal took place. With the addition of 3% additive more than 14% mullite formation occurred after sintering. A significant improvement in the formation of mullite in the sintered masses was also observed in the presence of CoO additive. More than 10% improvement in density as well as flexural strength and about 5% improvement in fracture toughness of the sintered compacts were observed in the presence of the CoO additive.

Keywords: Mullite, Di-Phasic gel, CoO additive, Mechanical properties, Microstructure.

1. Introduction

Mullite has achieved considerable importance as an engineering material for its several remarkable physico-chemical properties. These properties include low thermal expansion and thermal conductivity, good thermal and chemical stability, high melting point, low creep rate, reasonable toughness and strength, good thermal shock resistance, adequate infrared transparency etc [1-4]. For these beneficial properties mullite ceramics are widely used in the production of heat resistant materials in heat insulation, refractories, heat exchanger, turbine blades, spacecraft components, computer chips etc. [5, 6]. Composition wise 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 atoms per unit cell, varying between 0.25 and 0.59 [7, 8]. Although there have been different methods existing for the synthesis of mullite, during the last few years chemically synthesized active precursors have been widely employed for the processing of mullite. These precursors are converted to mullite at a relatively low temperature range from ~850$^\circ$C to ~1350$^\circ$C [9-11] and this type of mullite is known as “chemical mullite” [12]. Among several methods, sol-gel process is one of the widely used processes for the synthesis of chemical mullite. By sol-gel process generally three sequences for mullite crystallization may be observed [13], (i) mullite may be crystallized from the amorphous phase directly for single phase gel (ii) mullite can be crystallized via spinel phase (iii) mullite also can be crystallized from the reaction of discrete crystalline or semicrystalline alumina and amorphous silica from diphasic gels. Researchers have been focusing on the diphasic gel precursors for its relatively higher activity for the synthesis of advanced materials. Diphasic gels as type–II precursors of mullite [14] consist of pseudo boehmite and amorphous silica at room temperature. During heat treatment boehmite forms δ-Al$_2$O$_3$, this reacts with amorphous silica to form mullite above 1250$^\circ$C. Type-III diphasic gel are non-crystalline up to 980$^\circ$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$^\circ$C, which later reacts with amorphous silica to form mullite at < 1250$^\circ$C. Different transition metal oxides have been shown to have favourable mineralizing effect on the formation of mullite ceramics from the precursor materials. Ferreira da Silva [15] observed that presence of manganese ion can induce mullitization at lower temperature from Al$_2$O$_3$-SiO$_2$ gel. Martisius and Giraitis [16] ob-
erved that copper oxide as an additive can decrease the transformation temperature of kaolinite to mullite by 200°C. Kong et al [17] observed that V2O5 accelerated the mullite phase formation, while Nb2O5 and Ta2O5 inhibited the mullitization. Baudin and Moya [18] investigated the influence of TiO2 on the sintering and microstructural evolution of mullite and observed that addition of TiO2 under the solubility limit enhanced the initial sintering and grain size in mullite whereas an amount in excess of that limit inhibit sintering and drastically increased the total porosity and mean pore size. Nass et al [19] studied on the influence of chromium ion on homogeneity of gels and on mullite formation and mean pore size. Nass et al [19] studied on the influence of limit inhibit sintering and drastically increased the total porosity and grain size in mullite whereas an amount in excess of that close to 3:2 (x=1/4) for Al2O3 gel was calcined at 800°C from value for the formation of mullite as -5.8 kCal at 1422°C and Moya [18] investigated the influence of TiO2 and microstructural evolution of mullite and observed that additive for reducing the formation temperature for the conversion of kaolinite to mullite [21, 22]. Schneider and Vasudevan [23] worked on manganese doped mullites synthesized from metal organic starting materials by a modified sol-gel technique at low temperature and suggested that up to ca 6wt% Mn2O3 can enter the mullite structure. Dayal et al [24] determined the free energy value for the formation of mullite as -5.8 kCal at 1422°C from the oxide components under equilibrium condition in the system CoO-Al2O3-SiO2. Schneider [25] observed that cobalt doped mullite produced electron paramagnetic resonance (EPR) spectra with signals near geff = 4.9 and 2.2.

In the present investigation the effect of CoO on the crystallization of mullite from Al2O3-SiO2 bi-phasic gel precursor powder derived from inorganic salts was investigated by analyzing the microstructure and mechanical properties of sintered products.

2. Experimental

The aluminosilicate hydrogel was synthesized from the starting materials Al(NO3)3. 9H2O (analar grade) and liquid sodium silicate (analar grade with sp. Gr. 1.6 and molar ratio of Na2O: SiO2 =1:3) Chemical compositions of the starting materials is given in table 1. 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/minute. Silica sol was prepared by ultrasonic dispersion of the generated silicic acid (5% w/v) in aqueous phase. The silica sol formed was mixed with 10% (w/v) Al(NO3)3.9H2O solution stoichiometrically to attain a molar ratio close to 3:2 (x=1/4) for Al2O3 and SiO2 in the mix at pH=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 and characterized by chemical analysis, measurement of surface area and bulk density. The results are given in table 2. The gel was calcined at 800°C for a period of 2 hours. The calcined gel was properly pulverized in a pot mill and thoroughly mixed with CoO (Reagent Grade) additive in different ratios by co-grinding. The composition of the different batches is given in table 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 hours 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 30mm 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. [26]. XRD pattern of the samples was taken with a Rigaku X-ray diffractometer with Cu target (MiniFlex, Japan). Scanning electron microscopic investigation of the samples was carried with FEI Quanta microscope (US).

3. Results and Discussion

Silica sol is a positively charged colloid and after generation by ion exchange process, it did not show any tendency of polymerization. When silica sol was mixed with Al(NO3)3 solution, the solution became acidic. With the addition of ammonium hydroxide non-simultaneous formation of the aluminium hydroxide and polysilicic acid gels took place and therefore, the formed aluminosilicate gel was bi-phase in nature. In this system discrete aluminium hydroxide gel particles were likely to be distributed uniformly in the high molecular weight polysilicic acid gel network.

Table 1. Chemical constituents of the ingredients (wt %).

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Na2O</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 2. Physicochemical properties of the hydrogel.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2 (wt %)</td>
<td>17.86</td>
</tr>
<tr>
<td>Al2O3 (wt %)</td>
<td>48.23</td>
</tr>
<tr>
<td>Ignition Loss (wt %)</td>
<td>33.91</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.27</td>
</tr>
<tr>
<td>Sp. Surface area (m²/g)</td>
<td>170</td>
</tr>
</tbody>
</table>

Table 3. Batch composition of the samples.

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Al2O3-SiO2 Hydrogel</th>
<th>CoO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>97</td>
<td>3</td>
</tr>
</tbody>
</table>

The precursor gel powder is expected to have considerable surface activity as it had a very low bulk density (0.27g/cm³) and
a considerably high surface area (70m²/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 (molar ratio of Al₂O₃/SiO₂ 3.18) to minimize the formation of glassy phase after sintering. After synthesis no deviation was observed from the parent batch composition in the synthesized material as in the alumina rich zone all of the silica in the composition was likely to get converted to mullite phase.

In the FT-IR spectra of the gel sample (Figure 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)₃ and they grew rapidly side by side to form diphasic gel [27]. 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 [28]. 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 [28, 29]. 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.

The additive CoO used in the present investigation has a periclase (rock salt) structure with a lattice constant of 4.2615 Å [30]. According to CoO-Al₂O₃-SiO₂ phase diagram, within the compositional range selected in the present investigation, cobalt silicate and cobalt spinel (cobalt aluminate) are likely to form in the presence of CoO. In the presence of excess Al₂O₃ and SiO₂ cobalt silicate and cobalt aluminate is converted to thermodynamically more stable mullite in the following way,

\[
3(\text{Al}_2\text{O}_3,\text{SiO}_2) + 2\text{CoSiO}_4 \rightarrow 2\text{CoO} + 3\text{Al}_2\text{O}_3,2\text{SiO}_2 + 3\text{SiO}_2
\]

\[
2(\text{Al}_2\text{O}_3,\text{SiO}_2) + 3\text{CoAl}_2\text{O}_4 \rightarrow 3\text{CoO} + 3\text{Al}_2\text{O}_3,2\text{SiO}_2 + 2\text{Al}_2\text{O}_3
\]

In other words, CoO reduces the energy barrier for the formation of mullite via the intermediate formation of active cobalt silicate and cobalt aluminate. The presence of cobalt silicate and cobalt aluminate was also detected by XRD studies.

Again, the 3d⁻ electrons of Co²⁺ in an octahedral crystal field are split from the energetic ground state to the low spin state (t₈)²(eg)⁶. The eg electron occupies the dₓ²₋ᵧ² orbital and not the dₓz⁻y² orbital. The dₓz electron can repel the electrons of the respective oxygen ligands. As a result the octahedron’s z-axis is lengthened. Therefore a deformation in oxygen octahedral takes place. This distortion is known as Jahn-Teller distortion [31]. Moreover the cationic size of six-coordinated Co²⁺ under low spin state is 83.8 pm [32] which is larger than that of Al³⁺ [53 pm]. Therefore mullite lattice undergoes deformation lattice deformation in the presence of Co²⁺. This deformation is responsible for expansion of lattice along b-axis and shortening along a-axis. Earlier studies also indicated that Co²⁺ existed in octahedral coordination in mullite structure [25].

The incorporation of Cobalt (II) ions into the aluminosilicate samples also can induce defect in the structure in the following way,

\[\text{CoO} + \alpha\text{Al}_2\text{O}_3 \rightarrow \text{Co}_\alpha\text{Al}_{2\alpha} + \alpha\text{Al}_2\text{O}_3 + O_\alpha^{0\alpha} + 0.5V_0^{0\alpha}\]

The defect generated can assist in further densification of the material during heat treatment.

Formation of both cobalt silicate and cobalt aluminate phases was observed from the XRD diffractogram of the samples (Figures 2A and 2B). The lattice parameters of the doped and undoped mullite crystals were calculated following the process as described by Krishna Murthy and Hummel [33]. The calculated values of lattice parameters of undoped mullite were like the following, \(a=7.5238\text{Å}, b=7.6789\text{Å}\) and \(c=2.8671\text{Å}\) with lattice volume of 165.65(Å³). For the sample with 3% CoO the lattice parameters were like the following, \(a=7.5321\text{Å}, b=7.7314\text{Å}\) and \(c=2.8892\text{Å}\) with cell volume 168.24(Å³). Therefore a volume expansion of about 1.56% took place for mullite crystal as a result of doping with 3% CoO. From the cell parameters it was observed that the maximum deviation took place along the b-axis of the crystal lattice. Again the relative percentage of mullite also increased with the increase in the both CoO content and sintering temperature. The mullite content in different batches was estimated using XRD technique following the procedure described by Chung [34]. It was observed that with the addition of 3% CoO about 14.5% more mullitization was achieved at the highest sintering temperature of 1600°C (Figure 2C).

Grain size of the sintered mullite samples were calculated from the XRD profiles using Scherrer’s equation. In this case it has been assumed that both stress and particle size leads to size broadening of the diffraction peaks. Instrumental contribution was also taken into consideration for peak broadening [35, 36]. The modified Scherrer’s equation as given below has been used for this purpose.

![Figure 1. FT-IR Spectra of The Gel Sample](image-url)
From the SEM micrographs of the sintered samples (Figures 3A and 3B) it is apparent that un-doped sol-gel mullite formed very small crystallites. The incorporation of cobalt ions in the sol-gel mullite induced tabular crystal growth parallel to the crystallographic c-axis. With the increase in the cobalt ion content in mullite, formation of more equi-axed but smaller sized crystallites was observed. With the increase in the sintering temperature also the size of the crystallites reduced. The microstructure became more cohesive with the increase in the additive content.

\[ \beta_i^2 = \left( \frac{0.9\lambda}{D \cos \theta} \right)^2 + (4\varepsilon \tan \theta)^2 + \beta_i^0 \]  

(2)

\( \beta_i \) represents total broadening, \( \varepsilon \) is the strain, \( \lambda \) is the wavelength, \( \theta \) is the diffraction angle, \( \beta_i \) is the instrumental broadening, \( D \) is the average particle size. By a least square method the experimentally observed broadening of several peaks were used to compute the average particle size \( D \) and the strain \( \varepsilon \) simultaneously.

The average crystallite size calculated for sample with 3% CoO content was found to be 4.4 μm at a sintering temperature of 1400°C, 3.5μm at a sintering temperature of 1500°C and 1.9 μm at a sintering temperature of 1600°C. The corresponding values of average microstrains were 0.0028 at 1400°C, 0.0017 at 1500°C and 0.0008 and 1600°C respectively.
The variation in bulk density and apparent porosity (Figures 4 and 5) of the samples with sintering temperature has been shown in figures 3 and 4. From the figures it is clear that CoO exhibited a positive effect on the densification of the mullite ceramics. About 15% improvement in the density was observed with 3% CoO content at the highest sintering temperature under the investigation. The apparent porosity was reduced by 35% in the presence of 3% additive at the sintering temperature of 1500°C.

The flexural strength and fracture toughness (Figures 6 and 7) of the samples also increased in the presence of CoO additive. It can be related to the development of interlocked elongated crystal in the microstructure. The grain boundary did not contain noticeable glassy phases. The effect was more pronounced for the batch containing 2% additive. The flexural strength increased by 13% with the addition of 2% additive at a sintering temperature of 1500°C. Similarly the fracture toughness of the samples was also improved in the presence of CoO additive. Fracture toughness increased by about 5% with the addition of 3% additive at the sintering temperature of 1600°C. 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 [37].

Figure 3B. Scanning Electron Micrograph of the sintered gel samples with 3% cobalt oxide additive(i): sintered at 1400 °C (ii) sintered at 1500°C (iii) sintered at 1600°C

Figure 4. Variation in Bulk Density with Firing Temperature

Figure 5. Variation in Apparent Porosity with Firing Temperature

Figure 6. Variation in Flexural Strength with Firing Temperature
4. Summary and Conclusion

Mullite ceramics was synthesized from the biphasic aluminosilicate gel precursor, which was prepared by the colloidial interaction of silicic acid and Al(NO₃)₃ solution. The gel powder possessed very low density and high surface area and consisted of separate non-linked units of alumina and silica gel. CoO was used as sintering additive for the processing of mullite ceramics in different proportions. CoO promoted the formation of mullite by the interaction between Al₂O₃ and SiO₂ via the intermediate formation of cobalt silicate and cobalt aluminate. Different mechanisms like, interaction with the alumina and silica sub lattices, Jahn-Teller effect, anionic vacancy formation of liquid phase at higher temperature etc. was put forward to explain the favourable effect of CoO. The crystallite size of mullite was also modified by CoO. The mechanical properties of the sintered masses were also improved significantly due to improved microstructure and favourable phase compositions.

References