Effect of Solution pH on Mullite Phase Formation from a Diphasic Precursor Powder

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Available online at: www.austceram.com/ACS-Journal

Abstract:
The effects of solution pH on the properties of the stoichiometric diphasic mullite precursor powder have been investigated. Mullite precursor powder was prepared by precipitating a mixture of aluminium nitrate solution and fume silica in ammonia solution maintaining three different pH conditions. The precursor powder made at pH-6, pH-8 and pH-10 were studied by TG-DSC analysis to know about the thermal decomposition behavior. Phase analysis of the precursor powder and calcined powder at different temperatures was done by XRD study. The presence of different functional group in the precursor powder and calcined powder is confirmed by the FTIR study. Lastly the particle morphology, tendency of agglomeration and surface area was investigated by microstructure analysis, particle size distribution and surface area analysis respectively. It was found that the desired mullite phase formation and other properties of powder precursor are very much pH dependent.

Keywords: Precursor powder, Solution pH, Mullite, Phase analysis, Microstructure,

INTRODUCTION:
Mullite is a well-known, stable compound in the alumina-silica system. It has exceptional properties like excellent high-temperature strength, outstanding chemical and thermal stability, low thermal expansion coefficient and very good creep resistance [1-3]. Several processes already reported for the preparation of the mullite precursor powder. It was found that many factors like particle size, degree of mixing, Al/Si ratio, the presence of an impurity phase, etc. affect the mullitization process [4-5]. The definite reaction leading to mullite formation is also dependent on starting material and synthesis process. Precursor pH is another important factor related to mullite formation from stoichiometric composition [6]. Mullite precursor powder can be prepared in monophasic or diphasic form by sol-gel or coprecipitation technique. This classification of monophasic and diphasic precursor powder has been done on the basis of chemical homogeneity [7]. In case of monophasic powder, chemical homogeneity is at the atomic level, and direct mullitization is possible at a temperature as lower as 980 °C. In diphasic powder, the homogeneity is in the nanometer or micrometer level, and mullite formation temperature increases to more than 1200 °C [8-10]. Many pieces of researches have been done to study the effect of solution pH on the single phase mullite precursor powder formation [11]. The studies related to the effect of pH on mullitization from stoichiometric mullite composition are limited. Therefore, in the present study attempt is made to investigate the effect of solution pH on mullite formation from a stoichiometric diphasic mullite powder precursor.

METHODS AND PROCEDURE
Mullite precursor powder of stoichiometric composition 3Al₂O₃·2SiO₂ was prepared by reacting aluminium nitrate solution with fumed silica at three different pH conditions. Aluminium nitrate solution was prepared by dissolving aluminium nitrate nonahydrate of purity 99% (E-Merck India) in distilled water. Calculated amount of fume silica was mixed with the solution in such a proportion that it maintains Al₂O₃:SiO₂ molar ratio 3:2 in the final product. Chemical precipitation was done by reverse strike using 25% NH₃-water (analytical grade) as a precipitant. Three batches of precursor powder (Batch-A, B and C) were prepared by varying the pH
in the range of 6-10 to study the effect of the pH change on the mullite phase formation. The prepared precipitates were then filtered and washed repetitively with hot water to remove the extraneous soluble impurities. The solid mass left were then dried at 110±10 °C. The detail synthesis process is represented in flow sheet-1. The batch name and corresponding precipitation pH is given in table-1.

**Flow Sheet-1** Synthesis process of Mullite powder precursor

<table>
<thead>
<tr>
<th><strong>Batch</strong></th>
<th><strong>pH</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch A</td>
<td>6</td>
</tr>
<tr>
<td>Batch B</td>
<td>8</td>
</tr>
<tr>
<td>Batch C</td>
<td>10</td>
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</table>
The prepared precursor powder was then characterized by different characterization techniques like DSC-TG, Particle size analysis, Surface area analysis, Dilatometer study, XRD, FTIR and FESEM. Thermal analysis was done using simultaneous DSC/TG system- Netzsch Germany STA449C/4/MFC/G, under an inert atmosphere. FTIR analysis and phase analysis were carried out by FTIR spectrometer- Perkin Elmer, SQ 300S, wavelength range- 400-4000 /cm, and RIGAKU JAPAN/ ULTIMA-IV using Cu Kα radiation. Surface area and particle size analysis were carried out by using BET surface area analyser (Quantachrome/ AUTOSORB-I) and Zeta sizer- Particle size analyzer (Malvern/Nano ZS) respectively. The linear expansion or shrinkage was measured by using Dilatometer (Netzsch, Germany, DIL 402C). Morphology of the prepared powders was studied by using a Field Emission Scanning Electron Microscope (Nova Nano SEM/ FEI 450). Precursor powders were then heat treated at different temperatures, and all the heat-treated powders were subjected to XRD and IR analysis to study the phase formation mechanism.

RESULTS AND DISCUSSION

Thermal analysis

The thermogravimetric curves of the precursor powder of batch-A and B are shown in figure-1. The thermal analysis curves for batch B and C are similar so, the curves for batch-C is not shown here.

![Figure-1 TG curve of batch-A and B precursor powder.](image1)

From the figure, it is clear that the weight loss in batch B and C is almost same (~27%) except for batch-A, where the weight loss is higher around 33% and completed at 700 °C. In case of batch-B and C though the weight loss is less compared to batch-A, but it continued up to higher temperature 900 °C. All the powder samples show three stages weight losses. The weight losses and the corresponding endothermic peaks shown in the DSC curves (figure-2) are due to the loss of moisture, dehydration of silicic acid gel and dehydration and dehydroxylation of alumina hydroxide gel.

![Figure-2 DSC curve of batch-A and B precursor powder.](image2)

At the higher temperature range a wide exothermic hump in the temperature range 800-1000 °C is attributed to Al-Si spinel / γ-Al₂O₃ formation. In batch-A sample, a weak exothermic peak at 1090 °C probably indicates the transformation of this γ-Al₂O₃ to other transition phase alumina. At further higher temperature mullite phase is expected to be form as a result of the reaction between these transition alumina phases with free silica. In batch-B and C samples, the two overlapping exothermic peaks in the temperature range 1200 °C – 1300 °C indicate two step mullite crystallization reactions. In case of diphasic precursor powder, sometimes on calcinations, segregation of alumina-rich and silica-rich region is formed. The alumina rich region at higher temperature converted to mullite through the transformation of Al-Si spinel phase [12]. The first peak is assumed to be responsible for this phenomenon. The second peak is due to the mullite formation by the reaction between transient alumina and silica rich amorphous phase.

Fume silica when dispersed in an aqueous medium, it initially forms a stable sol. Here water molecules form H-bond with silanol group (Si-OH) present on the silica surface. It generates a solvation layer that coats each silica particle. The firm bonding of these water molecules within this salvation layer is then expected to produce a short range repulsive force preventing particle coagulation as shown in figure-3 [13-14].
When this is mixed with the aluminium nitrate solution, then the solution became acidic, the pH value is around 2. At this pH, the surface of the silica particle is positively charged. When this solution is mixed with ammonium hydroxide, the pH rises, and the formation of aluminium hydroxide gel and polysilicic acid occurs. Thus, the formed gel is diphasic in nature. At high pH above pH 7 up to 10, silica dissolves as silicates. The hydrous silica particles are now negatively charged. So they repel each other, and there is no polymerization of hydrolyzed silica and evolution of water [16]. This phenomenon is probably related to the lower amount of weight loss for the powder prepared at higher pH. Here though the weight loss is less around 27%, but it continued up to the higher temperature around 900 °C. At higher pH around 8-10 due to condensation of Al³⁺ ion througholation and oxolation mechanism a polynuclear hydroxide formed [17, 18].

\[
[M(H₂O)₆]^{3+} \leftrightarrow [M(H₂O)₅OH]^{2+} + H^+ \quad \text{……..(1)}
\]
\[
[(H₂O)₅M–OH–M(H₂O)₅]^{5+} \quad \text{……..(2)}
\]

Because of this polycondensation, particle size is bigger at higher pH. In the acidic condition, the equilibrium of equation-(1) shifted towards left thus inhibit poly-condensation. Therefore, the delayed weight loss in the diphasic gel formed at higher pH may be due to the trapping of water molecule within this large polymer [19].

3.2 Phase analysis
The X-ray diffraction study of batch-A, B and C and their calcined powder has been done, and the corresponding diffraction patterns are shown in figure-4, 5 and 6 respectively.

From the patterns, it is clear that bayerite and gibbsite are the two distinct phases that are present in the powder precursor prepared at the different pH condition. After calcining at 600 °C the gel transform to a mixture of an amorphous phase and γ-alumina. Further heating leads to the formation of other

![Figure 4 XRD patterns of Batch-A (G-Gibbsite; B-Bayerite; γ -Gamma Alumina; δ-Delta Alumina; θ-Theta Alumina; α-Alpha Alumina; κ'- Kappa Alumina).](image-url)
transition phase aluminas like \( \delta \)-alumina and \( \theta \)-alumina though silica remains amorphous. At 1200 °C, batch-B exhibits mullite phase but for batch-A, there is no mullite phase formation though some new transition alumina phases and the stable \( \alpha \)-alumina phase is found to form. The X-ray diffraction pattern of precursor powder and calcined powder of batch B and C are almost similar.

In the DSC curve, the broad exothermic peak above 900 °C which is indicated either for Al-Si spinel formation or \( \gamma \) alumina formation appears from the XRD study as the \( \gamma \)-alumina phase. The Al-Si spinel, which is a solid solution of \( \gamma \) alumina and silica, is very difficult to distinguish from the \( \gamma \)-alumina phase. The presence of two overlapping exothermic peak in the DSC trace for mullite powder prepared, at higher pH, in the temperature range 1200 °C-1300 °C supports the presence of Al-Si spinel phase along with \( \gamma \) alumina phase. Many authors showed that [20-22] spinel phase contained a certain quantity of silica incorporated in \( \gamma \)-alumina, so it quickly converted to mullite phase around 1200 °C. The pure \( \gamma \)-alumina phase at higher temperature turned to other transition alumina phase and subsequently reacts with the amorphous silica to form mullite. This two-step mullite formation may be one of the reasons for the presence of higher amount of mullite in batch-B calcined at 1200 °C.

The presence of transition alumina phases at 1200 °C is quite unusual but not impossible. Particularly in stoichiometric composition the coexistence of amorphous silica, metastable alumina and mullite is already reported [12, 21, and 23]. Only in alumina rich composition above 1200 °C, \( \theta \) alumina decomposed and converted to mullite and corundum [24]. Many researchers showed the presence of amorphous silica stabilized transition alumina phases in mullite precursor powder at and around 1200 °C [25, 26]. It is already established that the apparent stability domain of transition aluminas are enlarged by the addition of silica [27].

Figure-5 XRD patterns of Batch-B (G-Gibbsite; N-Nordstrandite; B-Bayerite; \( \gamma \)-Gamma Alumina; \( \theta \)-Theta Alumina; m-Mullite).

In the presence of fumed silica, if \( \gamma \)-alumina is heat treated at 1200 °C then \( \theta \) alumina, and other transition alumina phases are formed. In the absence of fumed
silica, at the same temperature $\alpha$ alumina is the main product [28]. The mechanism of retarding alumina phase transition is considered as follows. In this diphasic powder during thermal treatment as the transition alumina phases formed then the amorphous silica forms a coating on the surface of the $\gamma$-alumina particle and prevents particle contact. This phenomenon helps to suppress the coagulation of $\gamma$-alumina particle and in turn retard phase transition [28].

Figure-6 XRD patterns of Batch-C (G-Gibbsite; N-Nordstrandite; B-Bayerite; $\theta$-Theta Alumina).

Figure-7 Schematic representation of amorphous silica stabilised transition alumina [28].
**FTIR analysis**

Figure 8 shows the FTIR spectra of mullite precursor powder of batch-A and B. The broad and strong absorption band in the range 3000 cm\(^{-1}\) – 3600 cm\(^{-1}\) in both cases, indicates stretching region of OH group and H\(_2\)O molecule. The deconvolution of this absorption region reveals four different bands due to bridging H\(_2\)O, bridging OH groups and non-bridging H\(_2\)O, non-bridging OH groups [29]. The absorption band around 3531 cm\(^{-1}\) and 3456 cm\(^{-1}\) represent the stretching mode of OH group and H\(_2\)O molecule respectively without any hydrogen bridging. On the other hand, the OH stretching mode around 3294 cm\(^{-1}\) and H\(_2\)O stretching mode around 3078 cm\(^{-1}\) requires strong hydrogen-bonding. A similar type of water and hydroxide bridging is also found in the glass structure [9, 29].

During heat treatment, hydrogen-bonded molecular water and hydroxide groups eliminated comparatively quickly, and a minor amount of non-bridging OH group and water molecules remains at a higher temperature.

The absorption band around 1639 cm\(^{-1}\) and 1386 cm\(^{-1}\) is due to bending moment of the water molecule and presence of nitrate group [9]. The presence of absorption band around 820 cm\(^{-1}\) and 1077 cm\(^{-1}\) are assigned to the Si-OH stretching mode and bending mode. The stretching mode of Al-O-Al linkage and Si-O-Si linkage of the gel network are observed around 734 cm\(^{-1}\) and 474 cm\(^{-1}\) [30]. It indicates the presence of Al-O-Al linkage and Si-O-Si linkage in the precursor powder. The absence of Si-O-Al linkage in the same powder implies the inhomogeneity and diphasic nature of the powder precursor.

**3.4 Morphology study**

Figure 9A, 9B and 9C shows the FESEM micrographs of batch A, B and C. From the micrograph, it is clear that the powder is in agglomerated state and contains a dense aggregate of the primary particle. The size of the agglomerates and primary particles are finers for the powder prepared at lower pH. The morphology of the prepared precursor powder is affected very much by the solution pH condition. In the basic condition, pH ≥ 8 there is a tendency to polycondensation and formation of larger primary particle [31].

Figure-10 shows the dilatometric study of batch B in the temperature range room temperature to 1400 °C. From the graph, it is observed that the sample size remains almost constant up to around 1100 °C. Above 1100 °C shrinkage occurs. The shrinkage is due to the initiation of densification process of mullite powder.
Figure-9 FESEM micrograph of batch A, B and C powder precursor.

Figure-10 Dilatometric graph of batch-B.
3.5 Surface area analysis
The BET surface area plots of different batches are shown in figure-11. The influence of solution pH on surface area of prepared mullite precursor powder is shown in figure-12. The surface area of the prepared powder is found to increase here with increasing pH of the solution.

![BET surface area plot of batch-A, B and C.](image1)

3.6 Particle size analysis
Particle size distribution of the prepared mullite precursor powder of different batches is shown in figure-13. From the figure, it is found that the size distribution is mono-modal with the average particle size 712 nm, 570 nm and 430 nm for the batch A, B and C respectively. The observed particle size is much higher than the size found from the micrograph. This deviation is due to agglomerate formation. The larger agglomerate size for batch-A sample supports the result of lower surface area for the same.

![Plots of surface area vs precipitation pH for different batches.](image2)
CONCLUSIONS
Mullite precursor powder in the diphasic gel form has been prepared at three different pH conditions. The outcomes of this study are summarized as follows:

- It is found from the study that the surface area, primary particle size, agglomeration formation and thermal decomposition are very much affected by the change of solution pH during precipitation.
- In higher pH samples though the primary particle size is larger, but the agglomeration is less.
- At 1200 °C, batch-B exhibits mullite phase but for batch-A, there is no mullite phase formation though some new transition alumina phases and the stable α-alumina phase is found to form.
- The higher reactivity of batch B powder is related to its larger surface area and earlier phase transition of intermediate alumina phases.

ACKNOWLEDGEMENT
This is a part of M. Tech (by research) thesis, the work is funded by NIT Rourkela. The authors would like to thank every faculty, technical stuff and research scholar of Ceramic Engineering department NIT Rourkela for their cooperation.

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