CHAPTER 5

EFFECT OF PYROLYSED RICE HUSK IN THE NITRIDATION OF SOL-GEL DERIVED SILICA AND BOEHMITE

5.1 INTRODUCTION

Sol-gel technology deals with the preparation of inorganic material via chemical routes. Sol-gel route enables the materials to be mixed on a molecular level and then brought out of the solution either as a colloidal gel or a polymerised macromolecular network whilst retaining the solvent. This solvent is desiccated off leaving a solid with a high level of fine porosity (Kerch et al 1990). So high is the porosity that these solids possess very high surface area and therefore surface free energy and it is this property that enables the solid to be sintered and densified at much lower temperatures than one would expect in the normal processing of the same material. For instance, a temperature of 1750°C is required to fuse silica SiO₂, yet a dense solid can be prepared from a gel at 1100°C.

It is characteristic of single oxides in the sol gel process that a portion of the cross-linking reactions takes place at relatively low temperatures and often in solution. Equations 5.1 to 5.3 show some of the network forming reactions.
The variations of the network can be introduced by controlled hydrolysis-polymerisation reactions of metal alkoxides. This permits structural variation without compositional alteration. Glass formation by melting, however, does not allow a significant variation in network parameters, except by compositional changes. It is to be observed that in sol-gel technology, the drastically reduced synthesis temperature is achieved only at the cost of expensive and highly reactive starting materials (alkoxides).

The special advantages of sol-gel are:

1. Extreme purity since extremely pure starting materials are available
2. Perfect stoichiometry and dosability since the bonds can be preformed in solution
3. Very fine spherical particles (which can hardly be produced by milling)
4. A narrow particle size distribution

Sol-gel processing has become a useful method for preparing large varieties of glasses and glass ceramics. Tetraethoxysilane (TEOS) has been one of the most utilised raw materials for this purpose. Kinetic studies of the
hydrolysis and condensation reactions of alkoxides often deal with the alkoxide-water-alcohol system (Chou and Lee 1993).

5.1.1 Nitridation of Sol-Gel Derived Silica

High temperature oxidation-resistant materials have gained significant importance in recent years as they have applications as protective coatings on materials such as carbon-carbon composites to inhibit oxidation at elevated temperatures. Constant efforts of the various materials scientists have revealed that incorporation of nitrogen or carbon into the silica network leads to the synthesis of a class of compounds called oxycarbide and oxynitride, with excellent mechanical, physical and chemical properties (Zhang and Pantano 1990). For example, silicon oxynitride possesses resistance to thermal shock, corrosion, creep and oxidation and it has a coefficient of thermal expansion matching to that of carbon-carbon composites.

Recently there is much interest for the incorporation of carbon into silica-based glasses to form Si-C bonds in a homogeneous network (Kamiya et al 1990). The homogeneous network, whose composition is $\text{Si}_x\text{O}_{2(1-x)}$, $0 \leq x \leq 1$, can be referred to as a silicon oxycarbide glass. It is formed by a random array of mixed silicon oxycarbide units $[\text{Si}_z\text{O}_{4-z}\text{C}_z]$ with $0 \leq z \leq 4$ and carbon units $[\text{C}_{4}\text{Si}_4]$. The presence of tetra coordinated carbon units is expected to lead to a stiffer and more constrained network resulting in an important improvement of the elastic modulus, hardness, viscosity, density, and glass transition temperature. Moreover, the C-containing network should have a lower tendency toward devitrification. Thus, it is evident that silicon oxycarbide glasses can be regarded as a modification of silica glass groups suitable for high temperature applications, when the use of $\text{SiO}_2$ is limited because of its high
devitrification rate or low viscosity and consequently high creep rates. Raman et al (1993) have nitrided silica gels with additives such as hexamethylene tetramine, carbon fibre, glucose etc., at different temperatures employing a mixture of nitrogen gas and liquid ammonia.

The synthesis of nitrogen-containing glasses is generally accomplished by the melting silica and silicon nitride at high temperatures in a nitrogen atmosphere. It is obtained by bubbling ammonia through the molten glasses or by chemical vapour deposition. The scientific advancement in this research field has been hindered mainly by experimental difficulties faced in the fabrication of silicon oxycarbide glasses by the melting process. Recently, the successful synthesis of amorphous Si-O-C glasses by the sol-gel route has been reported in the literature (Baney 1984). According to this processing approach, the oxycarbide glass is obtained by hydrolysis of modified silica gel containing organic groups. The sol-gel process using metal alkoxides as starting materials has a high potential for preparing inorganic oxide ceramics. Tetraalkyloxysilanes such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) have been widely used to fabricate silica-related materials.

Polymeric silica gel may be produced by polycondensation of hydrolysed tetraethoxysilane (TEOS) under acidic conditions through a sol gel process. This method is particularly attractive to ceramic scientists since high purity silicate glasses can thus be prepared at much lower temperatures than required by the conventional melting method. (Mackenzie 1984 & Sakka 1984) Although sol gel method has its advantages, a high tendency to crack during drying of bulk silica gels is often encountered. Crack formation during the drying is caused primarily by the stress generated in the gel due to the capillary
forces. Therefore, it has been suggested that fracture can be avoided by making gels with larger pore size and by using solvents of low surface tension and low volatility.


5.1.2 Nitridation of Sol-Gel Derived Boehmite

Alumina refractories are widely used in the metallurgical and ceramic industries as bricks, monolithic materials, kiln furniture, crucibles, etc. The incorporation of mullite into alumina is a way to improve its thermal shock resistance, because of the lower thermal expansion coefficient of the mullite phase. Ceramic fibres have been used for modification of toughness because they increase fracture energy due to their high elastic modulus and strength. Kim and Na (1995) have reported an increase in toughness, strength and thermal shock resistance when ceramic fibres are used in a gas filter for high temperature applications. The basic systems studied were clay bonded SiC-mullite and Al\(_2\)O\(_3\)-mullite with carbon black (to improve filtering efficiency). Komarneni et al (1997) have studied the formation of porous \(\alpha\)-alumina ceramics from boehmite and rice flour. Radonjic et al (1993) have studied the relationship between the microstructure of boehmite gels and their transformation to \(\alpha\)-alumina. Boccaccini et al (1999) has studied the activation energy for the mullitisation of a diphasic gel obtained from fumed silica and boehmite sol.
The mechanism of mullite formation from the reaction of alumina and amorphous silica was believed to be via nucleation and growth from the siliceous matrix with the dissolution and diffusion of alumina to reach saturation composition for mullite nucleation. Mullite is also an intermediate phase in the formation of non-oxide ceramics (sialons). This reaction involved the formation of mullite under non-oxidising atmospheres and in the presence and absence of carbon (Mackienzie et al 1996).

The infiltration of porous compacts with suitable infiltrants is one way of introducing additional phases into the body. The compact subsequently can be calcined to yield a dense composite with one or more additional phases. The infiltration process has been successfully used to introduce mullite into alumina. (Marple and Green 1989). Studies on the development of mullite/ SiAlON/alumina composites have been studied by Albano and Scian (1997). In this work, several aspects related to the processing of SiAlON/alumina composites with several infiltrants are studied in detail. Schmucker and Schneider (1999) has studied the transformation of X- sialon to mullite.

5.1.3 Design of Experiment

The incorporation of nitrogen into the silica gel is tried by preparing the gels with compounds containing carbon. Silica gels by the sol-gel technique with various concentration of pyrolysed rice husk were nitrided at four levels of temperature namely 800°C, 900°C, 1000°C and 1100°C in a tubular furnace in an atmosphere of flowing nitrogen. Thermo gravimetric analysis and differential scanning calorimetry were carried out on the gel. The nitrided products were characterised by infrared, X-ray diffraction and surface area studies to investigate the extent of nitrogen incorporation and the effect caused
Figure 5.1 Flow chart for the thermal nitridation of sol-gel derived silica with pyrolysed rice husk.
by the nitrogen introduction on the physico-chemical properties of the gel. Additives such as charred rice husk, glucose and dextrose were added, pelletised, and nitrided at 1400°C in flowing nitrogen for 6 hours. The X-ray diffractogram, IR spectrum and pore size distribution of these three pellets were compared.

An attempt is made to synthesis nitrided mullite from boehmite sol and pyrolysed rice husk. Here rice husk was chosen to incorporate carbon and nitrogen into the system to enhance the gas filtering efficiency of the product. The gels were fired in a vacuum furnace in nitrogen atmosphere at 1400°C. The thermo gravimetric and differential thermal analyses were carried out. The nitrided products were characterised for XRD, IR, and pore size distribution studies. The microstructural studies by SEM were also carried out.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 Nitridation of Sol-Gel Derived Silica

The flowchart for the nitridation of sol-gel derived silica is shown in Figure 5.1. All chemicals used in the present investigation were of analytical grade. 20 ml tetraethoxy silane (TEOS, Fluka, 98% pure) was mixed with 65 ml of distilled water, 20 ml ethanol (99% pure), and 2.5 ml concentrated nitric acid and 10ml dimethyl formamide. The mixture was stirred well for 4 hours at 40°C using a magnetic stirrer. The required amount of additive was added to it and stirred vigorously. The amount of additive was varied in steps of 2.5 g of pyrolysed rice husk and the gels were termed as G1, G2, G3, and G4 & G5 respectively. The mixture was stirred well for 2h at 60°C using a magnetic stirrer, gelled and dried in an oven for two days at 80°C. The samples G1, G2, G3, G4 & G5 were heat treated to 800°C, 900°C, 1000°C and 1100°C in an
atmosphere of nitrogen. The nitrogen flow started from 50°C with 2.0 l/minute flow rate. The heating rate was 7°C/minute. The soaking time was one hour in the respective temperature. The samples were cooled from the respective temperature to 600°C at a rate of 2°C/minute and from 600°C to 100°C at a rate of 8°C/minute.

The decomposition behaviour of gel sample G3 was investigated using a thermo gravimetric analyser (Perkin Elmer TGA-7) and a differential scanning calorimeter (Perkin Elmer DSC-7) X-ray diffraction data were recorded using an X-ray diffractometer. (Phillips, Holland). IR spectra were recorded for gels G1, G2, G3, G4 & G5 fired at 800°C and 1000°C. The potassium bromide disk technique was used in the present IR study. The infrared spectra were recorded by means Fourier transformed infrared spectrometer. (Bruker IFS 66v FTIR spectrometer) The various spectral bands were identified from the literature. The baseline technique was adopted for the determination of absorbencies. Surface area measurement was carried out by BET method (Micromeritics Chemisorb 1200 and Nova 1000).

Gels were prepared with 2.5g of additives of charred rice husk, glucose and dextrose and designated as S1, S2 and S3 respectively. The dried gels were crushed into powders, pressed into a pellet, and fired in a flowing nitrogen atmosphere at 1400°C for 6 hours. XRD and IR spectra were carried out for the samples S1, S2 & S3. Pore size distribution by mercury porosimetry was carried out.
5.2.2 Nitridation of Sol Gel Derived Boehmite

The experimental procedure is shown in the Figure 5.2. Commercially available reagent grade aluminium isopropoxide was used as the starting material for preparing boehmite sol. Aluminium iso-propoxide was hydrolysed in hot water. The molar ratio of alkoxide to water was maintained at 1:100. Hydrolysis was carried out in double distilled water by stirring continuously for one hour. 0.3mole of HNO₃ per mole of alkoxide was added as the peptising agent. The peptisation was carried out under vigorous stirring for 90 minutes. Throughout the experiment the temperature was maintained at 80°C. In order to avoid any loss of water, hydrolysis and peptisation were performed under refluxing conditions. During hydrolysis, the solution was milky white. This white dispersion turned to transparent pale blue sol after the addition of nitric acid. About 1000ml sol of boehmite yields 50 grams of boehmite powder. The amount of α-Al₂O₃ recovered from 50 gms of boehmite powder was approximately 37.5 gms.

Five mix compositions of pyrolysed rice husk and boehmite powder at the weight ratios of 1:9, 2:8, 3:7, 4:6 and 5:5 were taken and were named as M1, M2, M3, M4 and M5 respectively.

Pyrolysed rice husk was added to the boehmite sol and stirred vigorously for few hours. In addition, the temperature was gradually raised to 110°C and the sol was allowed to form gel and oven dried at 110°C for 48 hours. These mixtures were fired at 1400°C for 6 hours in a static nitrogen atmosphere. Thermal studies of green sample (M4) was carried out using Setsys TG-DTA 18 from room temperature to 1400°C at a flow rate of 10 K/minute under helium atmosphere. The phase formation of the powders fired at 1400°C
Figure 5.2  Flow chart for the thermal nitridation of sol-gel derived derived boehmite with pyrolysed rice husk.
with various rice husk concentrations was determined by X-diffractometer using CuKα as the source and Ni as the filter. The bond formation was determined from FTIR spectra, in the range of 4000-400 cm⁻¹. The measurement was made on sample M4 mixed with KBr at 1:50 by weight. The mercury porosimetry and scanning electron microscope were used to study the pore size distribution and porous microstructure.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Nitridation of Sol-Gel Derived Silica

5.3.1.1 Thermal Analysis

The weight loss of samples G1, G2, G3, G4 and G5 at temperatures 800°C to 1100°C is shown in Figure 5.3. It is seen that weight loss increases with increasing amount of pyrolysed rice husk. Particularly for composition G5, weight loss is very high compared to other samples. The TGA and DSC curves of sample G3 are presented in figures 5.4 and 5.5. The weight loss between 100°C and 300°C with a peak at 188°C is assigned to the evaporation of OH groups, dimethyl formamide and to the decomposition of additives. Thereafter TGA curve shows negligible weight loss up to 800°C. The above observations are supported by the DSC studies which show endothermic at 119°C assignable to the evaporation of water, alcohol, dimethylformamide and hydroxyl groups and a exothermic peak at 199°C is attributable to the decomposition of the additives in the gel sample. TGA of sample G3 (heating rate 20°C/min) indicates a total weight loss of 28.4%, whereas sample G3 when fired at 7°C/min and a soaking of one hour shows a weight loss of 36.7%.
Figure 5.3  Weight loss Vs pyrolysed rice husk of sol-gel derived silica
Figure 5.4 TGA curve of G3
Figure 5.5 DSC curve of G3
5.3.1.2 Phase and Structural Analysis

The X-ray diffractograms are taken for all the samples and shown in the Figures 5.6, 5.7, 5.8, 5.9 and 5.10. The X-ray powder patterns of the powders are amorphous. It is seen that samples fired at 1100°C show crystallinity. It is also seen that nitrided samples prepared with a gel precursor containing high amount of rice husk (G5) reveal crystalline silica.

FTIR spectra show the possible formation of bonds and the relative concentration of each species by their spectral position and peak intensity.

Table 5.1 Results of IR spectra of G1, G2, G3, G4 and G5.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Silanol band (3500cm⁻¹)</th>
<th>Si-O-Si band (1070cm⁻¹)</th>
<th>Si-O-Si band (800cm⁻¹)</th>
<th>Si-C band (465cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>3491.5</td>
<td>1089.3</td>
<td>799.5</td>
<td>458.4</td>
</tr>
<tr>
<td>G2</td>
<td>3492.4</td>
<td>1089.1</td>
<td>797.3</td>
<td>464.0</td>
</tr>
<tr>
<td>G3</td>
<td>3492.8</td>
<td>1092.1</td>
<td>800.2</td>
<td>463.8</td>
</tr>
<tr>
<td>G4</td>
<td>3491.8</td>
<td>1086.9</td>
<td>800.0</td>
<td>457.6</td>
</tr>
<tr>
<td>G5</td>
<td>3452.7</td>
<td>1088.6</td>
<td>795.8</td>
<td>460.9</td>
</tr>
<tr>
<td>1000°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>-</td>
<td>1103.1</td>
<td>795.3</td>
<td>465.9</td>
</tr>
<tr>
<td>G2</td>
<td>-</td>
<td>1101.2</td>
<td>695.5</td>
<td>465.8</td>
</tr>
<tr>
<td>G3</td>
<td>-</td>
<td>1105.4</td>
<td>792.5</td>
<td>465.0</td>
</tr>
<tr>
<td>G4</td>
<td>-</td>
<td>1101.2</td>
<td>791.6</td>
<td>467.7</td>
</tr>
<tr>
<td>G5</td>
<td>-</td>
<td>1099.1</td>
<td>792.8</td>
<td>473.8</td>
</tr>
</tbody>
</table>

The infrared spectra of G1, G2, G3; G4 & G5 fired at 800°C and 1000°C is shown in Figures 5.11 and 5.12 from which it can be stated that
Figure 5.6  XRD pattern of G1
Figure 5.7  XRD pattern of G2
Figure 5.8  XRD pattern of G3
Figure 5.9 XRD pattern of G4
Figure 5.10 XRD pattern of G5
Figure 5.11 IR spectra of G1, G2, G3, G4 & G5 fired at 800°C
Figure 5.12  IR spectra of G1, G2, G3, G4 & G5 fired at 1000°C
The spectra of the gel also show characteristic bands of silanol group around 3500 cm\(^{-1}\) and the depth of this peak increases with increasing pyrolysed rice husk content. It is noticed that this band is completely absent in sample fired at 1000°C.

The absorption peaks at 1300-1500 cm\(^{-1}\) due to residual ethoxy groups are absent indicating complete hydrolysis (West and Hench 1995).

The nitridation at 800°C gives peak in the region 1086.9 cm\(^{-1}\) and at 1000°C gives peak in the region 1099.1-1105.4 cm\(^{-1}\). The symmetric bending and symmetric stretching vibrations of O-Si-O and Si-O-Si are observed at 450 cm\(^{-1}\).

The gel nitrided at 1000°C shows the broadening of the band around 1000 cm\(^{-1}\), which is due to the incorporation of nitrogen into the gel network.

If the silica tetrahedral is connected to form a chain, ring or a more complicated structure they give rise to absorption band occurring at 800 cm\(^{-1}\). This band represents Si-C and Si-N stretching bands.

In G5 fired at 1000°C, a small peak is observed around 620 cm\(^{-1}\) which may be due to the crystalline silica (Cooper 1992).

The X-ray diffractograms are taken for all the samples (S1, S2 & S3) and the results are shown in the Figure 5.13. The X-ray powder patterns of the samples show that they are crystalline. The major phase in all the samples is that of silica and minor phase is that of silicon nitride. Table 5.2 shows the results of IR spectra.
Figure 5.13  XRD pattern of S1, S2 & S3
Table 5.2 Results of IR spectra of S1, S2 and S3.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Si-O-Si band (1070 cm(^{-1}))</th>
<th>Si-O-Si band (800 cm(^{-1}))</th>
<th>Si-C band (620 cm(^{-1}))</th>
<th>Si-C band (465 cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>1094.8</td>
<td>790.6</td>
<td>621.0</td>
<td>483.4</td>
</tr>
<tr>
<td>S2</td>
<td>1093.4</td>
<td>790.3</td>
<td>621.1</td>
<td>481.4</td>
</tr>
<tr>
<td>S3</td>
<td>1096.3</td>
<td>789.0</td>
<td>621.1</td>
<td>469.8</td>
</tr>
</tbody>
</table>

The results of the FTIR spectra of samples S1, S2, S3 are shown in Figure 5.14, from which it can be stated that

1. The nitridation at 800°C gives peak in the region 1086.9 cm\(^{-1}\) and at 1000°C gives peak in the region 1093.4-1096.3 cm\(^{-1}\). The symmetric bending and symmetric stretching vibrations of O-Si-O and Si-O-Si are observed at 450 cm\(^{-1}\).
2. The gel nitrided with pyrolysed rice husk shows the broad and deep band around 1094.8 cm\(^{-1}\), which is due to the incorporation of nitrogen into the gel network.
3. If the silica tetrahedra are connected to form a chain, ring or a more complicated structure they give rise to absorption band occurring at 800 cm\(^{-1}\). This bands represents Si-C and Si-N stretching bands.
4. A band is observed around 620 cm\(^{-1}\), which may be due to the formation of crystalline silica (Cooper 1992).
Figure 5.14 IR spectra of S1, S2 & S3
5.3.1.3 Surface Area and Pore Size Analysis

The variation of surface area with compositions of G1, G2, G3, G4 and G5 at 800°C and 1000°C is shown in the Figure 5.15. It is observed that the surface area decreases with increasing pyrolysed rice husk. The samples fired at 800°C show higher surface area than samples fired at 1000°C. The adsorption and desorption behaviour of samples G1 and G5 fired at 800°C in Figures 5.16 and 5.17. There is no remarkable hysteresis in G1 whereas there is some amount of hysteresis in G5. The surface area of sample G1 is 265.9 m²/g with an average pore size of 12.5 Å whereas the surface area of G5 is only 8.43 m²/g with an average pore size 32.08 Å.

Singh and Pantano (1996) have obtained silicon oxycarbide gels with high surface area and glasses from mixtures of methyl dimethoxysilane (MDMS) and tetraethoxysilane (TEOS) through acidic hydrolysis and condensation. A surface area of 275 m²/g and an average pore size of 30 Å were obtained by them for a 50% MDMS-50% TEOS glass at 800°C under a flowing argon atmosphere. However, the surface area of pure sol-gel derived silica was 1.3 m²/g.

Raman et al (1993) also have confirmed that the surface area decreases with increase in temperature. The specific surface area by BET method shows that the nitrogen incorporation involving the removal of OH groups in the silica network leads to densification and this causes a decrease in surface area. It is also evident that nitrogen incorporated at 1000°C reduces the surface area considerably when compared to the nitrogen introduced at 800°C.
Figure 5.15 Surface area Vs pyrolysed rice husk of sol-gel derived silica.
Figure 5.16 Pore size distribution of G1 fired at 800°C (BET method)
Figure 5.17 Pore size distribution of G5 fired at 800°C (BET method)
The pore size distribution of samples S1, S2 and S3 were analysed by mercury porosimetry and are shown in figure 5.18. Table 5.3 shows the comparative analysis of S1, S2 and S3.

Table 5.3 Pore size distribution studies of S1, S2 and S3

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pore volume (%)</th>
<th>Median pore diameter (μm)</th>
<th>Bulk Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>16.4</td>
<td>3.27</td>
<td>1.46</td>
</tr>
<tr>
<td>S2</td>
<td>11.8</td>
<td>1.65</td>
<td>1.88</td>
</tr>
<tr>
<td>S3</td>
<td>16.5</td>
<td>3.49</td>
<td>1.76</td>
</tr>
</tbody>
</table>

It is seen that composition S1 shows higher porosity with lower bulk density compared to other compositions.

5.3.1.4 Microstructure

The SEM micrographs of S1 are shown in Figure 5.19. Figure 5.19(a) shows the porous nature at lower magnification. Figure 5.19 (b) shows the fibre morphology of rice husk.

5.3.2 Nitridation of Sol-Gel Derived Boehmite

5.3.2.1 Thermal Analysis

Figure 5.20 shows the TGA and DTA graph of green sample (M3). The DTA curve shows a distinct endothermic peak at around 150°C. This corresponds to the drying process accompanied by the removal of physically adsorbed water molecules from boehmite and volatiles in rice husk. The crystallisation is indicated by exothermic peak (DTA) at 1250°C. The total
Figure 5.18 Pore size distribution of S1, S2 & S3 fired at 1400°C (Mercury porosimetry method)
Figure 5.19 SEM micrographs of S1
(a) Porous morphology
(b) Fibrous morphology
Figure 5.20 TGA and DTA of M3
weight loss (TGA) is around 33%. The weight loss of boehmite with various weight % of pyrolysed rice husk is shown in figure 5.21.

5.3.2.2 Phase and Structural Analysis

The X-ray diffractograms were taken for all the samples (M1, M2, M3, M4 & M5) and are shown in the Figures 5.22, 5.23 and 5.24. The X-ray powder patterns of M1 and M2 shows a mixture of mullite and alumina phases. The X-ray powder pattern of M3 shows that the predominant phase to be mullite and minor phase corresponds to alumina. M4 and M5 show peaks corresponding to that of mullite.

The IR spectrum of M4 is shown in Figure 5.25 from which it can be stated that

1. In M4 the 1163.7 cm\(^{-1}\) is seen which confirms the major phase to be mullite (Okada and Otsuka 1990).
2. All characteristic peaks of mullite at 1163.7, 1132, 909, 833.2, 732.8 and 574.5 cm\(^{-1}\) confirm the presence of mullite (Sales and Alarcon et al 1996).
3. The peak at 1132 and 909 cm\(^{-1}\) belong to SiO bond from SiO\(_4\), peaks at 1163.7, 833.2 and 732.8 cm\(^{-1}\) are due to Al\(_{x}\)-O bond from AlO\(_x\) and 574.5 peaks are due to Al\(_{6}\)-O bond from AlO\(_6\).

5.3.2.3 Pore Size Distribution Studies

The bulk density of M1, M2, M4 and M5 is shown in Figure 5.26. The pore size distributions of M1, M2, M4 and M5 before and after nitridation is shown in Figure 5.27 and 5.28 respectively. The pore volumes of non-
Weight loss Vs pyrolysed rice husk of sol-gel derived boehmite

Figure 5.21

$y = 5.11x + 21.65$

$R^2 = 0.9935$
Figure 5.22  XRD pattern of M1 & M2
Figure 5.23  XRD pattern of M3 & M4
Figure 5.24 XRD pattern of M5
Figure 5.25 IR spectrum of M4
Figure 5.26 Bulk density of M1, M2, M4 and M5 before and after nitridation.
Figure 5.27  Pore size distribution of M1, M2, M4 & M5 before nitridation.
Figure 5.28  Pore size distribution of M1, M2, M4 & M5 after nitridation
nitrided green samples and nitrided samples containing different amounts of pyrolysed husk are illustrated in Figure.5.29. The nature of intrusion-extrusion spectra is compared with literature (Lee 1990). It is found that green compacts consist of interior voids, whereas nitride compacts have voids extending to the surface. Figure 5.30 shows the graph between average pore diameter and pore volume versus pyrolysed rice husk of nitrided boehmite. The pore volume apparently decreases dramatically after nitridation. The pore volume of green samples increases continuously with increase in rice husk content.

The fired samples M1 and M2 seem to be very porous compared to M3, M4 and M5. In M1 and M2, the phase formed is predominantly alumina and very little mullitisation takes place. In samples M4 and M5, the porous volume of the nitride samples is lesser than the green samples. This may be attributed to the effective mullitisation of samples M4 and M5. This is also confirmed by the bulk density of samples and the above facts are confirmed by XRD.

5.3.2.4 Microstructure

The SEM morphology is shown in Figure 5.31. Figure 5.31(a) reveals the porous morphology. Figure 5.31(b) shows the platelet morphology.

5.4 CONCLUSION

Porous silica gels containing carbon and nitrogen were prepared by addition of pyrolysed rice husk. A high surface area of 265m$^2$/g with average pore size of 12.5 Å was obtained. The increased thermal stability of the surface
Figure 5.29  Average pore volume of M1, M2, M3 & M4 before and after nitridation
Figure 5.30 Average pore diameter and pore volume Vs pyrolysed rice husk of nitrided boehmite
Figure 5.31  SEM micrographs of M4
(a) Porous morphology
(b) Platelet morphology
area due to the incorporation of carbon was demonstrated. This composition may be tried as catalyst supports and absorbents for non-oxidising reactions.

Porous mullite is prepared from sol-gel derived boehmite and pyrolysed rice husk. The mullitisation increases with increase in rice husk content. The mullitisation take place across the porous structure of rice husk and the porous morphology is obtained.