CHAPTER 3

FORMATION OF POROUS SILICON NITRIDE, SILICON CARBIDE-SILICON NITRIDE AND SIALON COMPACTS:
EFFECT OF RICE HUSK

3.1 INTRODUCTION

Porosity is a common microstructural feature in any ceramic body. In some cases, the porous phase is tailored to produce specific properties in the material. For many applications, ceramic materials with zero/minimum porosity are preferred. Hence, the raw materials processing and subsequent heat treatment are designed to achieve a product close to full density. With either scenario, the importance of accurate pore characteristics is evident. Although porosity is the main cause for the reduction of mechanical properties in brittle solids, the development of porous ceramics is essential in some industries (Sepulveda 1997). This need has originated primarily from the application and properties that result from incorporated porosity with a tailored structure – high permeability, high surface area, good insulating characteristics, high refractoriness, chemical resistance and long service life in severe environments. The search for porous ceramics with good mechanical properties has stimulated the development of several technologies. The properties of porous ceramics greatly depend on pore morphology, pore size and pore size distribution (Shipilova et al 1998).
There are many applications for porous ceramic filters. They are filters for high temperature gas purification, particulate filters for diesel emissions, filters for molten metals, devices where chemically resistant and permeable materials are required at high temperatures, membranes for separation processes or molecular sieves for chemical processes, sensors, catalyst carriers for chemical plants and automobiles and large surface areas for the exchange of ions and catalysis. Other uses of porous ceramics are refractories, thermal insulation, furnace linings, humidity sensors, gas detectors, thermistors, porous piezoelectric ceramics and biomedical developments that can be used for restitution of skeletal and dental functions.

3.1.1 Nitride Bonded or Self Bonded Silicon Nitride

Among the two types of silicon nitride products, namely, dense sintered silicon nitride (by sintering, hot pressing and hot isostatic pressing) and the porous reaction bonded silicon nitride (RBSN), the later has attracted the attention of ceramic researchers during last few decades mainly because of its near net shape forming capability as well as the lower production cost. However, the processing of porous silicon nitride requires longer nitriding times (20-100 hours), especially for thicker samples. Porous silicon nitride products are developed using the following two approaches. One is the nitridation of silicon compacts containing various amounts of silicon nitride as inert filler. This reduces the nitridation time. In the second approach, the post sintering of RBSN products containing appropriate sintering aids has been followed to minimize the large volume shrinkages associated with the sintering of silicon nitride powder compacts, which incidentally lowers the production costs associated with the machining process.
Focusing on to the first approach of nitriding of silicon containing silicon nitride as an inert secondary phase, very few investigations are presented in the literature. Falk et al. (1985) have extensively studied the nitridation of cold isostatically pressed (CIP) compacts of coarse (≤ 300 μm) silicon containing 30 to 50 wt% of fine (= 0.6 μm) silicon nitride. Gregory and Richman (1984) have investigated the role of addition of silicon nitride (≤ 30 wt%) on the reaction bonding of silicon compacts prepared by CIP. Huang et al. (1996) have studied the effect of addition of silicon nitride (0-40 wt%) on the reaction bonding of silicon compacts. Williams et al. (1984) have investigated the effect of silicon nitride grog (≤ 16 wt%) on the slip casting of silicon and its nitridation. Contrary to the above studies, where the effects of addition of silicon nitride (0-50 wt%) on the nitridation process have been investigated, Bhat and Roy (1992) have studied the nitridation of silicon in the Si₃N₄-Si system where Si₃N₄ is the major component with 10-40 wt% of silicon.

3.1.2 Nitride Bonded Silicon Carbide and RBSN-SiC Composites

Nitride bonded silicon carbide (NBSC) ceramics were prepared by nitriding silicon green bodies containing SiC grains of different grit sizes in a N₂ atmosphere between 1350 to 1450°C so that the Si₃N₄ formed insitu interlocks and bonds the SiC grains (Mukerji and Reddy 1980). Generally in NBSC, the amount of Si₃N₄ bonding phase varies from 5-45% and the remaining is the SiC phase. Si₃N₄ bonded SiC ceramics have generated a sustained interest for their use in the field of refractories as well as in the field of high temperature structural applications for a long time (Sonntag 1998). These ceramics are known to possess remarkable erosion, corrosion and chemical resistance at high temperatures as well as good thermal shock.
They find specific applications in metallurgical, chemical, ceramic and aerospace industries (e.g., as aluminium electrolytic reduction cell linings as molten metal thermocouple sheaths, as high temperature refractory bricks, as refractory crucibles, as kiln furniture, as rocket nozzles, as high temperature turbine blades and as hot gas filters, etc.) (Rozak 1995). The economic advantage of using low cost silicon powders compared to Si$_3$N$_4$ powders and the low reaction nitridation temperature are added attractions along with the distinct advantage of near net shaping capability while producing these materials for their intended applications.

Several investigators have prepared NBSC composites by the above method and have studied their mechanical, thermal, oxidation and corrosion properties. NBSC bodies with densities 2.5-2.7 g/cm$^3$ have been produced with flexural strength of 30-40 MPa. Si$_3$N$_4$-SiC refractories with 5-45% of silicon nitride bond produced by Reddy and Mukherji (1991) have room temperature modulus of rupture values in the range of 15 to 56 MPa. They also found that the strength increased with the increase of temperature of testing, while the thermal expansion decreased. These refractories are resistant to molten non-ferrous metals but are attacked by molten cast iron. Albano et al. (1994) have studied the influence of microstructure on the mechanical strength of NBSC products having 13-37% silicon nitride bond and correlated their mechanical property to the porosity present in them. Similarly, the microstructural analysis of NBSC has been studied by Edwards et al. (1995). Recently Park and McNallan (1995) have reported the high temperature mixed oxidation of NBSC in an oxidizing gas mixture containing 2.0% chlorine and found that SiC is selectively chlorinated leaving behind the porous matrix of silicon nitride.
Contrary to the above mentioned NBSC products, the reaction bonded silicon nitride (RBSN) reinforced with various forms of SiC, like particles, platelets, whiskers, filaments or fibers etc., have been more recently studied by many investigators (Kosmac and Janssen 1997). Such RBSN-SiC composites generally contain about 5-30% of SiC phase dispersed in the RBSN matrix and are much stronger and tougher than monolithic RBSN and they retain their room temperature properties up to 1400°C. The properties are mainly controlled by the microstructure and chemistry of the interface between the matrix and reinforcing agent.

3.1.3 SiAlON

Sialon and related solid solutions have been developed mainly during the last decade, and fully dense polycrystalline bodies can now be prepared by pressureless sintering techniques. It has been found that aluminium oxide up to 60 wt.% can be incorporated in the solid solution with out any major structural changes. This material forms part of a whole group of materials called sialons in which the building unit is the (Si, Al)(O, N) tetrahedron. They have a composition of Si$_6$-$_x$Al$_x$O$_2$N$_{8-x}$ where x can vary from 0 to 5. Sialon became very popular, as it appears to have all the desirable properties of silicon nitride plus the ability to be sintered by the usual ceramic or powder metallurgy techniques. To prepare sialon, combinations of two or more of the compound silica, alumina, silicon nitride and aluminium nitride were used.

Dense sintered solids with compositions in the Si-Al-O-N system were obtained by nitridation of a mixture of naturally occurring silica and aluminium powder at temperatures up to 1400°C followed by hot pressing at higher temperatures (Umebayashi and Kobayashi 1977).
Purified coal, organic polymers, graphite (carbon black) or rice husks are used as carbon sources. The amount of carbon must be controlled within the stoichiometric ratio of the reaction in order to obtain a single-phase \( \beta \)-SiAlON. Lee and Cutler (1979) have shown that the carbon content must be controlled within \( \pm 0.5\% \) to obtain \( \beta \)-SiAlON free from impurities. Extra carbon leads to the formation of silicon carbide and a shortage in carbon leads to the formation of \( \alpha \)-\( \text{Al}_2\text{O}_3 \). The addition of iron acts as a catalyst on the formation of both SiAlON and silicon carbide. Van Dijen et al have prepared \( \beta \)-SiAlON powder (\( \text{Si}_3\text{Al}_3\text{N}_3\text{O}_3 \)) from approximately stoichiometric mixtures of kaolin and carbon under a nitrogen flow in the temperature range of 1400 to 1500\(^\circ\)C. They have reported that the nitrogen flow rate has to be low; otherwise, mixtures of aluminium nitride, silicon nitride and alumina are formed.

Rahman and Saleh (1995) have reported the formation of \( \beta \)-SiAlON from rice husk and kaolin by firing at 1430\(^\circ\)C for 16 hours. Other phases like silicon carbide, aluminium nitride and mullite are absent. In the Si-C-N-O system, the temperature of formation of silicon carbide is reported in the range 1450-1600\(^\circ\)C. The variation may be due to the differences in the starting powder characteristics (purity, surface area and carbon content) and processing conditions employed.

Aluminium nitride does not form because alumina is more difficult to reduce than silica. Carbon and silica are in the naturally mixed form. Therefore, they readily react to form SiO and CO. Then the reaction between boehmite and silicon monoxide leads to the formation of mullite. As more and more silicon monoxide reacts with mullite, it leads to formation of SiAlON phase. Rahman and Saleh (1995) confirmed that sialon, \( \text{Si}_3\text{N}_4 \), \( \text{Al}_2\text{O}_3 \) and mullite are formed when fired for 16 hours at 1430\(^\circ\)C in nitrogen atmosphere.
3.1.4 Design of Experiment

The effect of addition of pyrolysed rice husk on density, pore size distribution and microstructure of silicon nitride compacts are studied. The property of the product made out of pyrolysed rice husk and silicon nitride is compared with that of the product made out of pyrolysed rice husk and silicon metal powders. Microstructure and pore size distributions are studied.

Aluminium metal powder is mixed with pyrolysed rice husk and fired at 800°C in a flowing nitrogen atmosphere. These samples were again fired at 1400°C for 6 hours in a static nitrogen atmosphere. XRD, IR and pore size distribution and scanning electron microscopy were used to study the phases formed.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Characterisation of Pyrolysed Rice Husk

The rice husk was washed thoroughly with double distilled water to remove water-soluble impurities. Then it was dried at 110°C for 24 hours to remove moisture. Then the pyrolysis was carried out in the absence of air at 700°C for three hours. XRD, IR and SEM of pyrolysed rice husk were taken.

3.2.2 Synthesis and Characterisation of Porous Silicon Nitride Compacts

The starting materials used in this work were pyrolysed rice husk, silicon nitride powders.
The compositions of the mixture made in this study were as follows:

1. Five mix compositions of pyrolysed rice husk and silicon nitride at the weight ratios of 1:9, 2:8, 3:7, 4:6 and 5:5 and named as SN1, SN2, SN3, SN4 and SN5 respectively.

2. Another mix composition of pyrolysed rice husk and silicon metal powders at the weight ratios of 5:5 and named as X5.

The experimental procedure is as shown in the figure 3.1. All the batches were mixed thoroughly in a ball mill for two hours. Then the mixtures were pelletized in a uniaxial-pressing machine at a pressure of 150 MPa. 2% PVA was used as a temporary binder. After drying, the pellets were fired in a vacuum furnace. The furnace was evacuated and backfilled with nitrogen gas at a pressure of 20 kPa. All the samples were fired at 1400°C for 6 hours.

X-ray diffraction studies were used to investigate the mineralogical composition. A diffractometer with Ni filtered Cu Kα radiation (Phillips, Holland) was employed in this study. The compositions SN4 were analysed by FTIR spectrophotometer using KBr pellet method. The microstructure of SN5 and X5 were analysed by scanning electron microscope. Mercury intrusion porosimetry (MIP) is used to obtain the pore size distribution and pore volume data. A maximum pressure of 300 MPa is applied. Values for contact angle and surface tension were taken as 130° and 0.485 N/m, respectively. (Poresizer 9320, micromeritics corp.)
Figure 3.1  Flow chart for the synthesis of porous silicon nitride compacts
3.2.3 Synthesis and Characterisation of Porous Silicon carbide-Silicon Nitride Compacts

The starting materials used in this work were pyrolysed rice husk, silicon carbide powders. The compositions of the mixture made in this study were as follows:

Five mix compositions of pyrolysed rice husk and silicon carbide at the weight ratios of 1:9, 2:8, 3:7, 4:6 and 5:5 and named as SC1, SC2, SC3, SC4 and SC5 respectively.

All the batches were mixed thoroughly in a ball mill for two hours. Then the mixtures were pelletized in a uniaxial-pressing machine at a pressure of 150 MPa. 2% PVA was used as a temporary binder. After drying, the pellets were fired in a vacuum furnace. The furnace was evacuated and backfilled with nitrogen gas at a pressure of 20 kPa. All the samples were fired at 1400°C for 6 hours. The experimental procedure is shown in the figure 3.2.

X-ray diffraction studies were used to investigate the mineralogical composition. A diffractometer with Ni filtered CuKα radiation (Phillips, Holland) was employed in this study. The compositions SC4 were analysed by FTIR spectrophotometer using KBr pellet method. The microstructure of SC5 was analysed by scanning electron microscope. Mercury intrusion porosimetry (MIP) is used to obtain the pore size distribution and pore volume data (Poresizer 9320, micromeritics corp.).
Figure 3.2 Flow chart for the synthesis of porous silicon carbide- silicon nitride compacts
3.2.4 Synthesis and Characterisation of Porous Sialon Compacts

The starting materials used in this work were pyrolysed rice husk and aluminium metal powders.

The compositions of the trials made in this study were as follows:

Five mixed compositions of aluminium metal powder and pyrolysed rice husk at the weight ratios 1:9, 2:8, 3:7, 4:6 and 5:5 and named as AL1, AL2, AL3, AL4 and AL5 respectively.

The experimental procedure is shown in figure 3.3. All the compositions were mixed thoroughly in a ball mill for one hour. 2.0% PVA was used as a temporary binder. All the compositions were pelletised in a uniaxial pressing machine at a pressure of 150MPa. After drying, the pellets were prefired at 800°C in a flowing nitrogen atmosphere. The nitrogen flow started from 50°C with 2l/minute flow rate. The heating rate was 7°C/minute with a soaking of one hour. The samples were cooled to 600°C at a rate of 2°C/minute and from 600°C to 100°C at a rate of 8°C/minute.

All the prefired pellets were again fired in a vacuum furnace. The furnace is evacuated and backfilled with nitrogen gas at a pressure of 20 kPa with a soaking of 6 hours. X-ray diffraction studies were used to investigate the phases present. A diffractometer with Ni-filtered CuKα radiation (Phillips, Holland) was employed for this study. The composition AL4 was analysed by FTIR spectrometer. (Bruker 66v FTIR Spectrometer). The microstructure of AL4 was analysed by scanning electron microscope. Mercury intrusion porosimetry was carried out on the pellets.
Figure 3.3  Flow chart for the synthesis of porous sialon compacts
3.3 RESULTS AND DISCUSSIONS

3.3.1 Pyrolysed Rice Husk

The XRD (Figure 3.4) confirms the amorphous nature of the pyrolysed rice husk. In the IR spectra of coked rice husk (Figure 3.5), all the three peaks of raw rice husk are retained but the peak at 800 cm\(^{-1}\) becomes stronger by slightly shifting to 790 cm\(^{-1}\). The peak at 1089 cm\(^{-1}\) has become broader unlike for raw rice husk. This is due to Si-O bonding or from a combination of silica and carbohydrates. Figure 3.6 shows SEM micrograph of pyrolysed rice husk. The fibrous nature is retained even after pyrolysis.

3.3.2 Porous Silicon Nitride Compacts

The weight loss vs. composition (with increasing pyrolysed rice husk content after firing) is as shown in figure 3.7. The curve satisfies the linear equation \(y = 1.665(x) + 2.029\) with \(R^2=0.951\).

3.3.2.1 Phase and Structural Analysis

The XRD of compositions SN1, SN2, SN3, SN4 and SN5 is as shown in figures 3.8, 3.9 & 3.10 respectively. The major phase detected by XRD in all the samples is \(\alpha\)-Si\(_3\)N\(_4\). The intense peaks in the direction (201), (210) and (102) belongs to \(\alpha\)-Si\(_3\)N\(_4\). The minor phase detected is \(\beta\)-Si\(_3\)N\(_4\).

The infrared spectrum of SN4 is shown in Figure 3.11 from which it can be stated that:
Figure 3.4  XRD pattern of pyrolysed rice husk
Figure 3.5 IR spectrum of pyrolysed rice husk
Figure 3.6  SEM micrograph of pyrolysed rice husk.
Figure 3.7 Weight loss vs pyrolysed rice husk of silicon nitride (SN) compacts.
Figure 3.8  XRD pattern of SN1 & SN2.
Figure 3.9  XRD pattern of SN3 & SN4.
Figure 3.10 XRD pattern of SN5.
Figure 3.11 IR spectrum of SN4.
1. The IR bands resulting from the deformation vibrations of Si-N-Si and N-Si-N groups appear at 598.5 and 682.8 cm$^{-1}$.
2. The bands appearing at 1035 cm$^{-1}$ is due to Si-N stretching vibrations.
3. The band at 490.9 cm$^{-1}$ is due to the vibrational modes of α-silicon nitride (Patel and Prasanna 1991).

3.3.2.2 Density and Pore size Distribution Studies.

Mercury porosimetry is an effective tool to study the pore size distribution of sintered compacts when the porosity is greater than 10% (Zheng et al 1992). Figure 3.12 shows the gradual decrease in bulk density with increasing pyrolysed rice husk content. It satisfies the linear equation $y = -0.0972x + 1.7868$ with $R^2 = 0.9977$.

The pore size distribution of samples SN1, SN2, SN3, SN4 and SN5 is as shown in Figure 3.13. Sample SN1 shows a unimodal pore size distribution with a small shoulder around 0.1 μm. In sample SN2, the height of the shoulder further reduces. In sample SN2 small amount of macro pores are formed around 60 μm. This peak further sharpens in SN3. These pores are formed due to the agglomeration in the compacts. In SN3, SN4 and SN5, a bimodal distribution is seen. In SN3, a sharp peak at 0.7 μm and the height of the peak gradually increases in SN4 and SN5. The gradual shift of pores towards lower pore diameters is seen.

The graph between average pore diameter and pore volume with composition is as shown in Figure 3.14. The average pore diameter and pore volume increases with pyrolysed rice husk content for SN1, SN2 and thereafter
Figure 3.12 Bulk density Vs pyrolysed rice husk of silicon nitride (SN) compacts

Pyrolysed rice husk content (Wt. %)
Figure 3.13  Pore size distribution of SN1, SN2, SN3, SN4 & SN5
Figure 3.14 Average pore diameter and pore volume Vs pyrolysed rice husk of silicon nitride (SN) compacts.
decreases with pyrolysed rice husk content for SN3, SN4 and SN5. The packing between the starting materials (silicon nitride particles and pyrolysed rice husk) is less due to the incompatibility between particles and fibres. The better packing is obtained as the pyrolysed rice husk content increases from SN3. This is due to the high aspect ratio of fibres obtained from rice husk. However, the total pore volume variation from SN1 to SN5 is between 42.39 and 39.74%.

3.3.2.3 Effect of Pyrolysed Rice Husk on the Nitridation of Silicon Nitride and Silicon

One more sample with equal amounts of pyrolysed rice husk and silicon metal powder were fired under identical conditions (Composition X5) Table.3.1 shows the comparative analysis of pore volume, median pore diameter and Bulk Density of samples SN5 and X5. Figure 3.15 shows the pore size distribution of X5.

Table 3.1 Comparison of SN5 and X5

<table>
<thead>
<tr>
<th>Type</th>
<th>Pore Volume (%)</th>
<th>Median Pore Diameter (μm)</th>
<th>Bulk Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN5</td>
<td>39.82</td>
<td>0.5475</td>
<td>1.404</td>
</tr>
<tr>
<td>X5</td>
<td>53.73</td>
<td>1.4152</td>
<td>0.979</td>
</tr>
</tbody>
</table>

It is interesting to note composition X5 gives a bulk density of less than 1g/cm³. The only disadvantage of this method is the presence of residual silicon (0.5%).
Figure 3.15  Pore size distribution of X5.
3.3.2.4 Microstructure

Figure 3.16 shows the SEM micrograph of porous nitride samples (SN5 (a) and X5 (b) samples. Figure 3.16(a) shows more equiaxed grains compared to Figure 3.16(b). The micrograph 3.16(b) shows a mixture of short and long rod morphology. In general, the microstructure consists of large interconnected open pores.

3.3.3 Porous silicon Carbide-Silicon Nitride Compacts

The weight loss of compositions with increasing coked rice husk content after firing is as shown in Figure 3.17. The curve satisfies the linear equation $y = 2.5479x - 0.2279$ with $R^2=0.9947$.

3.3.3.1 Phase and Structural Analysis

The results of the XRD patterns of compositions SCI, SC2, SC3, SC4 and SC5 are as shown in figures 3.18 and 3.19 respectively. The major phase detected by XRD in all the samples is $\beta$-SiC. The secondary phase detected is $\alpha$-Si$_3$N$_4$ and traces of silicon oxy nitride are present.

The infrared spectrum of SC4 is shown in figure 3.20 from which it can be stated that:

1. The IR bands resulting from the deformation vibrations of Si-O-Si and Si-O-C groups appear at 464.1 cm$^{-1}$.
2. The prominent characteristic band at 818.7 cm$^{-1}$ results from Si-C stretching vibrations.
Figure 3.16 SEM micrograph of (a) SN5 and (b) X5
Figure 3.17 Weight loss Vs pyrolysed rice husk of silicon carbide-silicon nitride (SC) compacts
Figure 3.18  XRD pattern of SC1, SC2 & SC3.
Figure 3.19  XRD pattern of SC4 & SC5.
Figure 3.20 IR spectrum of SC4.
3. A hump at 1203 cm\(^{-1}\) results from Si-O stretching indicating the presence of amorphous silica. The higher frequency of this band associated with Si-O stretching mode may arise from the fact that amorphous phase consists of a pure silica material surrounded by the SiC. However, there is only a small hump present in this region. This indicates that the amount of amorphous silica is very less (Raju and Verma 1997).

3.3.3.2 Density and Pore Size Distribution Studies

Figure 3.21 shows the gradual decrease in bulk density with increasing pyrolysed rice husk content. The curve satisfies a linear equation \(y = -0.1334x + 1.905\) with \(R^2 = 0.9327\) Figure 3.22 shows the pore size distribution of SC1, SC2, SC3, SC4, SC5. The SC1, SC3 and SC4 show a unimodal pore size distribution. In SC2 and SC4, a small peak is present in the higher side (65\(\mu\)m). This may be due to the agglomeration during mixing. The graph between average pore volume and pore diameter with composition is as shown in Figure 3.23. The range of variation of porous volume from SC1 to SC5 is between 20.90 to 46.22%. This is due to variation in the particle size of the starting precursor powders.

3.3.3.3 Microstructure

Figure 3.24 shows the SEM micrograph of SC5. The morphology is fibrous in nature. The micrograph shows a mixture of short and long rod morphology. The microstructure consists of large open pores and interconnected voids.
Figure 3.21  Bulk density Vs pyrolysed rice husk of silicon carbide-silicon nitride (SC) compacts
Figure 3.22  Pore size distribution of SC1, SC2, SC3, SC4 & SC5.
Figure 3.23 Average pore diameter and pore volume Vs pyrolysed rice husk of silicon carbide-silicon nitride (SC) compacts
Figure 3.24  SEM micrograph of SC5
3.3.4 Porous Sialon Compacts

When the aluminium is about 50 wt.% the excess aluminium metal is oozed out. Therefore, the analysis of AL5 is dropped. The weight gain of the composition with increasing aluminium content is shown in Figure 3.25. It follows a linear equation \( y = 6.42x + 5.75 \) with correlation coefficient of \( R^2 = 0.9397 \).

3.3.4.1 Phase and Structural Analysis

The XRD of compositions AL1, AL2, AL3, AL4 and AL5 are shown in Figure 3.26. The major phase detected by XRD in all the samples is \( \text{Si}_4\text{Al}_4\text{O}_4\text{N}_4 \). The secondary phase detected is \( \text{Si}_2\text{Al}_2\text{O}_3\text{N} \) and traces of \( \alpha\text{-Si}_3\text{N}_4 \) are present.

The infrared spectrum of AL4 is shown in figure 3.27 from which it can be stated that:

1. The IR bands resulting from the deformation vibrations of Si-N-Si and N-Si-N groups appear at 602.4 cm\(^{-1}\).
2. The bands appearing at 1019 and 808.3 cm\(^{-1}\) may be assigned to Si-N stretching vibrations.
3. The band at 490 cm\(^{-1}\) corresponding to the vibrational modes of \( \alpha \)-silicon nitride is absent (Patel and Prasanna 1991)
4. The IR bands observed at 808.3 cm\(^{-1}\) and 652.2 cm\(^{-1}\) are considered to be due to the Al-O and Al-N stretching vibrational modes (Hanna and Ghoneim, 1986).
Figure 3.25  Weight gain Vs aluminium powder of sialon (AL) compacts

\[ y = 6.42x + 5.75 \]
\[ R^2 = 0.9397 \]
Figure 3.26  XRD pattern of AL1, AL2, AL3 & AL4.
Figure 3.27 IR spectrum of AL4.
3.3.4.2 Density and Pore Size distribution Studies

The bulk density vs. composition is as shown in Figure 3.28. The bulk density increases with aluminium content. The curve satisfies the linear equation $y = 0.1489x + 0.8567$ with $R^2 = 0.9938$. This is due to the fact that higher the amount of aluminium, higher is the reaction rate to form Si-Al-O-N solid solution.

The pore size distribution of AL1, AL2, AL3 and AL4 is shown in the Figure 3.29. The peak shifts gradually towards lower pore diameter from AL1 to AL4. AL1 shows bimodal pore size distribution. One sharp maximum is observed about 1 µm and two other peaks at 0.35 µm and 0.045 µm (Zheng and Reed 1992). By comparing the area under the curves it is seen approximately, 50% pore volume is composed of pores around 1 µm. From sample AL2 onwards, the pores at 0.35 µm and 0.045 µm grow at the expense of pores around 1 µm. A small peak is seen at around 60 µm, which is due to agglomeration of particles during mixing. Figure 3.30 shows the average pore diameter and average pore volume vs. aluminium metal power. A gradual falls in average pore volume and pore diameter as the aluminium content of the composition increases.

3.3.4.3 Microstructure

SEM micrograph of AL4 (Figure 3.31(a)) shows ribbon morphology. The structure is uniform with short cylindrical rods (Figure 3.31(b)). The sample contains high volume of open and interconnected pores.
Figure 3.28  Bulk density Vs aluminium powder of sialon (AL) compacts
Figure 3.29  Pore size distribution of AL1, AL2, AL3 & AL4.
Figure 3.30 Average pore diameter and pore volume Vs aluminium powder of sialon (AL) compacts
Figure 3.31 SEM micrograph of AL4
(a) Ribbon morphology
(b) Rod morphology
3.4 CONCLUSIONS

1. Porous silicon nitride compacts are prepared from mixtures of silicon nitride and pyrolysed rice husk. However, the variation of pyrolysed rice husk brings down the bulk density only to 1.3 g/cm$^3$.

2. A bulk density of less than 1 g/cm$^3$ is achieved from mixtures of silicon and pyrolysed rice husk. This offers a good method compared to the above one in terms of cost. The only disadvantage is the presence of residual silicon.

3. Porous silicon carbide–silicon nitride compacts are prepared with a minimum bulk density of 1.23 g/cm$^3$.

4. The formation of sialon-based solid solution is confirmed by firing aluminium - pyrolysed rice husk mixtures in nitrogen atmosphere with a maximum bulk density of 1.45 g/cm$^3$ corresponding to 40 wt% of aluminium.