In the present investigation, efforts have been made to carry out pyrolysis of rice husks under different conditions with the aim to produce Si-based ceramics in their pure forms, which are industrially valuable products.
5.1. RICE HUSK AS A PRECURSOR

5.1.1 Raw Rice Husk (RRH):

The RH was collected from a local rice mill with the husk dimensions of 7–10 mm long, 1.5–2.0 mm wide and 0.10–0.15 mm thick. Dry raw RHs were washed thoroughly with water to remove the adhering soil and other contaminants present in them and then dried in the sunlight for 24 h. These were designated as raw rice husk (RRH).

a) Chemical analysis:

Chemical analysis of RRH was carried out as shown in the flow chart (Fig.5.1). The data are tabulated in Table-5.1.

![Flow chart of chemical analysis of raw rice husk](image_url)

Fig.5.1 Flow chart of chemical analysis of raw rice husk
Major constituents, as found, are volatile matter (mainly different hydrocarbons such as cellulose and lignin), ash (mostly silica and other inorganic impurities) and fixed carbon (due to pyrolysis of hydrocarbons). Initial heat treatment at 700°C/2h in N$_2$ atmosphere (0.5 kg/cm$^2$ pressure) gives the weight loss due to volatile matters, i.e., hydrocarbons (60.5 wt %). Physical appearance of the residual material is black due to the presence of carbon. The fixed carbon is determined during heat treatment in air at 680°C/48h. So, weight loss at this stage is due to carbon (20.6 wt %). Remaining ash (taken in a Pt-crucible) is treated with concentrated HF followed by heating in the water bath till complete evaporation, and the difference in weight is found as SiO$_2$ (18.2 wt %) with the small amount of impurities left in the crucible (0.7 wt %).
A detailed and systematic heat treatment of RRH was carried out by thermal analysis (TG/DSC) from room temperature to 1000°C (Fig 5.2). The TG curve clearly indicates that the thermal decomposition of RRH takes place in three different stages. In the initial stage, weight loss (~5 wt %) is observed up to 100°C, which is mainly due to the removal of physically-bound water. Maximum weight loss (~60 wt %) takes place in the second stage (250-350°C). DSC plot also shows two close exothermic peaks during this stage, due to two components of organic matters (cellulose and lignin) participating in the second stage of decomposition reaction, well-known as pyrolysis. This stage of decomposition is the loss of volatile compounds, followed by the pyrolysis of cellulose and lignin to the intermediates, which may be the organic material of smaller molecular weight. In the third stage, gradual weight loss in the TG is observed with no sharp DSC peak. Hence, the thermal decomposition mechanism of the rice husk in this stage is attributed to the further oxidation of carbon in the residual intermediate to form other volatile species, viz. tar and char. The final char mainly contains high-purity silica [7].
c) SEM analysis:

Fig. 5.3 Inner side of RRH

Fig. 5.4 (a) Outer epidermis of RRH
Fig. 5.4 (b) Outer epidermis of RRH

Scanning electron micrographs of RRH are shown in Fig. 5.3, 5.4(a) and (b). Figure 5.3 shows the inner epidermis of RH, which is smoother in comparison to the outer layer and has a lamella structure. Fig. 5.4 (a) and 5.4 (b) show the outer epidermis of RH, which is well organized and has a corrugated structure. The silica is mainly localized in the tough interlayer (epidermis) of the RH; mainly concentrated in protuberances and hair trichomes on the outer epidermis and also adjacent to rice kernel [16]. The morphology is different for the outer and inner surfaces of rice husk. The silica is mainly localized in the tough interlayer (epidermis) of the rice husk and also filling in the spaces between the epidermal cells.
d) FT-IR analysis:

Results obtained from the FT-IR spectroscopy of RRH are shown in Fig. 5.5. As can be seen, RRH contains several absorption bands, which have been assigned to individual structural units as listed in Table 5.2 [19].
Table-5.2 Absorption bands in the FT-IR spectra and their assignment

<table>
<thead>
<tr>
<th>Region (cm⁻¹)</th>
<th>Assigned to</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600 - 3100</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>3000 - 2850</td>
<td>C-H stetching</td>
</tr>
<tr>
<td>1600</td>
<td>Aromatic C=C vibrations activated by neighboring oxygen groups</td>
</tr>
<tr>
<td>1500 - 1415</td>
<td>C – H deformation</td>
</tr>
<tr>
<td>1500 - 1200</td>
<td>CH₂, CH₃, Si(CH₃), C(CH₃)</td>
</tr>
<tr>
<td>1500 - 1000</td>
<td>Aromatic C=C skeletal vibration</td>
</tr>
<tr>
<td>1360 - 1310</td>
<td>C-C and C-O skeletal vibration</td>
</tr>
<tr>
<td>1100 - 1000</td>
<td>Si – O stetching</td>
</tr>
<tr>
<td>460, 796, 1093</td>
<td>Characteristic of Si – O bonds</td>
</tr>
</tbody>
</table>

5.1.2 Acid-treated Rice Husk (ARH):

Acid leaching was performed by treating the RRH with dilute HCl (1:1) in distilled water for 1 h. It was then washed thoroughly with distilled water followed by treatment with dilute ammonia solution (10 vol. %) for 1 h to remove the traces of acid. The treated husk was taken out and washed thoroughly in distilled water followed by drying in air for 24 h. This was designated as acid-treated rice husk (ARH).

a) SEM analysis:

The ARH sample in Fig.5.6 shows slightly smoother layer around the protuberances and trichomes, and widening of parallel grooves between the protuberances can be observed, which may be due to the removal of inorganic impurities during the acid treatment.
5.1.3 Black Ash (BA):

Fig. 5.6 Outer epidermis of ARH

Fig. 5.7 SEM of Black Ash (BA)
The BA sample in Fig. 5.7 shows many residual pores distributed within the ash indicating the presence of highly-porous silica with a large internal surface area [7].

Results obtained from the FT-IR spectroscopy of BA are shown in Fig. 5.8. As can be seen, RRH contains several absorption bands, which have been assigned to individual structural units as listed in Table 5.2. The indication of dehydration is confirmed by the negligible intensity of the O-H stretching band (3600–3100 cm\(^{-1}\)) in BA when compared with that in RRH. Organic decomposition can be observed from the absence of a 2900 cm\(^{-1}\) band representing C-H absorption and peaks of CH\(_2\) and CH\(_3\) at 1500-1200 cm\(^{-1}\) has dramatically diminished. In addition, absorbance bands at 1600 cm\(^{-1}\) (C=C) and 1700 cm\(^{-1}\) (C=O) imply that there are some aromatic structures present in the BA.
5.2. EFFECT OF TEMPERATURE ON THE MORPHOLOGY AND PHASE TRANSFORMATIONS OF NANO-CRYSTALLINE SILICA OBTAINED FROM RICE HUSK

5.2.1 Introduction:

Husk is a major agricultural by-product of rice milling industry in a country like India. Rice husk (RH) is a potential source of energy and value-added by-products among the various biomasses [1-3]. Rice husk contains ash (70 to 85%), organic matter (mainly cellulose and lignin) and the inorganic remainders consisting of silica and metallic impurities, depending on plant variety, climatic conditions and geographic location [3]. Carbon-free white ash, as a source of high-grade amorphous silica, obtained from the rice husk has opened a new dimension for its utilization, especially for the production of silica [4]. Rice husk as a resource of silica has been reported since the early forties; but during the past few decades, rice husk has been considered to be an excellent source of the active form of silica, especially due to its amorphous nature [5, 6]. Silica from rice husk has been widely used in the production of activated silica, sodium silicate, potassium silicate, solar-grade silicon, magnesium silicide, silicon nitride, silicon carbide, silicon oxynitride, sialon, fuming silica and zeolite because of its high reactivity. Silica obtained from RH is also used in electronics, cement and polymer industries [6, 7]. Nano-crystallined silica powders, which can be obtained from rice husk, have many technological applications such as thixotropic agents, thermal insulators, composite fillers, etc. [8]. Rice husk is formed during the growth of rice grains in the development stage of the plant, and different inorganic constituents and other impurities are deposited to it. Removed during the refining of rice, these husks have no commercial interest as such. Another relevant factor is their low cost compared to large applicability, and their growing demand also reduces the disposal and environmental pollution problem. There have been several reports on the formation of silica from rice husk [9-12].

Della et al. [9] observed that active silica with a high specific area could be produced from rice husk ash after heat-treating at 700°C in air. Kalapathy et al. [10] used a method to produce silica with lower sodium content by adding silicate solution to pH 1.5 hydrochloric, citric and oxalic acid solutions until the pH was brought to 4.0. Kamath and Proctor [11] found that the rice husk could be dissolved in sodium hydroxide solution, and then titrated with acid to obtain silica gel.
The different varieties of activated silica were also obtained after calcinations of RH at 600°C followed by the chemical treatment under static and flowing atmospheres of air, argon and oxygen as reported by Yalcin and Sevinc, [12]. Rice husk is a potential source of nano-structured silica having average particle size 26 nm and specific surface area 250 m²/g as reported by Conradt et al. [13]. Liou, [7] has reported the production of nano-sized silica from RH with average particle size 60 nm with specific surface area 235 m²/g by pyrolysis of RH in air. The present section deals with the production of nano-crystallised silica prepared from the pyrolysis of rice husk, study of different phases of silica as formed and quantitative estimation of silica in the pyrolyzed products from XRD analysis. EDS analysis also confirms the presence of silica and other impurities present in pyrolysed products.

5.2.2. Experimental Details:

About 5g samples of RRH and acid treated rice husk (ARH) were taken in separate cylindrical alumina crucibles and introduced into a muffle furnace for pyrolysis at different temperatures varying from 700°C to 1100°C at an interval of 100°C for 2 h soaking time in static air and weight losses were measured after each pyrolysis by an electronic balance. The pyrolyzed products were analyzed by X-ray diffractometer (XRD). A Philips X-ray diffractometer (model PW 1830) with CuKα radiation through Ni filter was used. SEM-EDS (JSM-6480 LV, JEOL) were used to study the morphology and elemental analysis of specimens. Crystallite size was calculated from the XRD graph by using the Scherrer’s equation [14]:

\[
t = \frac{0.9 \lambda}{B \cos \theta}
\]

... (1)

where \( t \) is crystallite size, \( \lambda \) is wave length of CuKα target, \( B \) is angular width (in radians) at half the maximum intensity and \( \theta \) is Bragg’s angle. Again,

\[
B = (B_{\text{meas}}^2 - B_{\text{equip}}^2)^{1/2}
\]

Where, \( B_{\text{meas}} = \text{Measured FWHM (full width half maximum)} \), \( B_{\text{equip}} = \text{FWHM due to instrumental broadening} \).
The amount of silica (vol.%) was calculated by using the following equation [14]:

\[
\text{Volume \% of silica} = \frac{\text{Height counts of highest intensity silica peak}}{\Sigma[\text{Height counts of highest-intensity silica peak} + \text{Height counts of highest-intensity carbon peak}]} \times 100
\]  \quad (2)

5.2.3 Results and Discussion:

1. Heat Treatments of Raw Rice Husk (RRH) and Acid-treated Rice Husk (ARH):

Heat treatments of RRH and ARH were carried out systematically from 700-1100°C for 2 h in static air (Fig.5.9). The weight remaining was observed to be around 83% and 78.5% for RRH and ARH, respectively, for 700°C. This difference in weight loss (~ 4.5 weight %) is due to the removal of metal-oxide impurities in ARH during chemical treatment. The gradual decrease in loss of weight was observed up to 1000°C in case of RRH. But, in case of ARH, weight loss reduced drastically up to 800°C and it became stabilized from 900°C onwards. This stabilization in weight change is due to crystallization of the heat-treated product, i.e., ash (which is mainly composed of SiO₂). The transformation of amorphous SiO₂→ quartz → tridymite → cristobalite is responsible for the same (as revealed from the XRD plots) [15].
Fig. 5.9 Weight loss of RRH and ARH during calcinations at different temperatures

2. XRD Studies of Pyrolysed Rice Husk:
Pyrolyzed products of heat-treated RRH and ARH in air were phase analyzed by XRD, and the composite plots are shown in the Fig. 5.10 (a) and 5.10 (b), respectively. In Fig. 5.10 (a), the ash produced at 700°C mainly contains amorphous silica; displaying a typical flat characteristic peak (2θ ~ 22°) of α-quartz. Similar type of plot is also observed for the materials calcined at up to 900°C. Transformation of amorphous silica to quartz and tridymite becomes prominent at 1000°C. The complete transformation is observed at 1100°C with very strong peaks of quartz and tridymite with smaller peaks of SiC. The presence of SiC is observed at such a low temperature due to the reaction between highly amorphous and nano-sized silica and carbon; whereas carbon is detected in all calcined materials.

Pyrolyzed products of heated ARH in air were phase analyzed by XRD and the composite plots are shown in Fig. 5.10 (b). The ash produced at 700°C mainly contains amorphous silica; displaying a typical flat characteristic peak (2θ ~ 22°) of α-quartz. Similar types of plots are also observed for the materials calcined at up to 800°C. Transformation of amorphous silica to quartz and tridymite becomes prominent at 900°C. The complete transformation is observed at 1100°C.
with very strong peaks of cristobalite and tridymite with smaller peaks of SiC formed during heat
treatment. The presence of SiC is observed at such a low temperature due to the reaction between
highly amorphous and nano-crystallined silica and carbon; whereas graphitization of carbon is
detected from 900°C onwards.

Fig. 5.10(a) XRD of RRH pyrolysed at different temperatures (700-1100°C)
Fig. 5.10(b) XRD of ARH pyrolysed at different temperatures (700-1100°C)

Fig. 5.11(a) Crystallite sizes of the calcined RRH
Crystallite sizes of the calcined RRH and ARH materials were worked out using Scherrer's formula as shown in the Eq. 1. (Fig.5.11 (a) and Fig.5.11 (b)). Crystallite size at 700°C is around 4.8 nm and it increases with rise in calcination temperature (5.6 and 8.1 nm for 800 and 900°C, respectively). Drastic increase in the crystallite size (17 nm) is observed for the product calcined at 1000°C. Crystallite size becomes almost stable (18.6 nm) at 1100°C. The increase in crystallite size at higher temperatures is probably due to the agglomeration and sintering. In case of crystallite sizes (Fig.5.11 (b)) of the calcined ARH materials, crystallite size at 700°C is found out to be 31.28 nm and it increases with rise in calcination temperature up to 31.58 nm at 1100°C. Drastic increase in the crystallite size is observed for the product calcined at 800°C. Crystallite size becomes almost stable (31.58 nm) at 1100°C. This increase in crystallite size at higher temperatures is probably due to the agglomeration and sintering. Similar types of results were also reported by Ibrahim and Helmy [4]. The crystallite size of ARH was found to be larger than that of RRH. This may be due to the reason that, in absence of metallic impurities in ARH, the agglomeration takes place more rapidly and easily.

Quantitative estimation of silica (volume %) produced after calcinations of RRH at different temperatures is determined from XRD plots (Fig.5.12 (a)). The presence of silica decreases from...
31.2 volume% at 700°C to 17.8 vol. % at 800°C followed by an increasing trend (23.5 volume% at 900°C). With increase in temperature from 700°C to 800°C, the pyrolysis of hydrocarbons (mainly cellulose and lignin) becomes very prominent and fast, leading to fixed carbon [5]. Silica content (in weight %) decreases because of the increase in carbon content in the total ash. The oxidation of carbon and remaining hydrocarbons is very fast at temperatures beyond 900°C. Thus, silica content in the ash increases continuously and the amount of silica reaches to ~ 97 volume % at 1100°C. Quantitative estimation of silica (volume %) produced after calcinations of ARH at different temperature are also carried out from XRD plots (Fig.5.12 (b)). The presence of silica shows an increasing trend from 48.55 to 80.08 volume %. Silica content (in weight %) decreases because of the increase in carbon content in the total ash. The oxidation of carbon and remaining hydrocarbons is very fast, thus silica content in the ash increases continuously and the amount of silica reaches to ~ 81 volume % at 1100°C. The volume % of silica was found to be comparatively less in case of ARH than that of RRH. This may be due to the loss of silica during acid leaching.

Fig. 5.12(a) Quantitative estimation of silica (volume %) of RRH
3. SEM Studies and EDS Analysis:

Scanning electron micrographs of raw rice husk (RRH), acid-treated rice husk (ARH) and calcined rice husk (CRH) are shown in Fig.5.4, Fig.5.6 and Fig.5.13. Fig.5.4 shows the outer epidermis of rice husk, which is well organized and has a corrugated structure. The silica is mainly localized in the tough interlayer (epidermis) of the rice husk; mainly concentrated in protuberances and hair trichomes on the outer epidermis and also adjacent to rice kernel [16]. The ARH sample appears (Fig.5.6) slightly smoother around the protuberances and trichomes and widening of parallel grooves between the protuberances due to removal of inorganic impurities during acid treatment. CRH sample (calcined at 1100°C in air) shows many residual pores distributed within the ash indicating the presence of highly-porous silica with specific surface area 25.06 m²/g for RRH. This is due to the thermal decomposition of organic matters present in the RH; thus leaving a highly porous structure. So, the structure of RRH and ARH is globular as it is formed by the relatively stable Si-O carcass and the biomass assembled around it. After pyrolysis, globules are shrinked and densified due to the release of the volatile products;
but globular structure of the RH is preserved due to the high thermal stability of SiO$_2$ [17]. The physical appearance of the CRH is white in colour due to the presence of almost pure silica (Fig. 5.13(a) and Fig. 5.13(b)).

EDS analysis shows (Fig. 5.14(a) – (f)) the presence of different elements present in RRH, ARH and CRH. Levels of metallic impurities are reduced during chemical treatment as revealed from the Fig. 5.14(a), 5.14(c) and 5.14(e). But CRH sample mainly shows (Fig. 5.14(e) and 5.14(f)) the presence of silica with small amount of residual carbon and metallic impurity CaO. The increase in Ca content may be due to the coarsening of metallic impurities as reported elsewhere [18]. From chemical analysis, the major constituents are found to be volatile matter, fixed carbon, silica and very small amount of metallic impurities. Volatile matters are mainly hydrocarbons like cellulose and lignin.

Fig. 5.13 (a) SEM micrographs of calcined RRH at 1100°C
Fig. 5.13 (b) SEM micrographs of calcined ARH at 1100°C

Fig. 5.14 (a) EDS spectrum of RRH
Fig. 5.14 (b) Elements present in RRH (weight %) from EDS analysis

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>28.6</td>
</tr>
<tr>
<td>O</td>
<td>51.03</td>
</tr>
<tr>
<td>Na</td>
<td>0.64</td>
</tr>
<tr>
<td>Mg</td>
<td>0.06</td>
</tr>
<tr>
<td>Al</td>
<td>1.05</td>
</tr>
<tr>
<td>Si</td>
<td>18.76</td>
</tr>
<tr>
<td>K</td>
<td>0.36</td>
</tr>
<tr>
<td>Ca</td>
<td>0.22</td>
</tr>
<tr>
<td>Fe</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Fig. 5.14 (c) EDS spectrum of ARH
Fig. 5.14 (d) Elements present in ARH (weight %) from EDS analysis

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>40.4</td>
</tr>
<tr>
<td>O</td>
<td>40.54</td>
</tr>
<tr>
<td>Na</td>
<td>0.55</td>
</tr>
<tr>
<td>Al</td>
<td>0.05</td>
</tr>
<tr>
<td>Si</td>
<td>17.08</td>
</tr>
<tr>
<td>K</td>
<td>0.64</td>
</tr>
<tr>
<td>Ca</td>
<td>0.73</td>
</tr>
<tr>
<td>Fe</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Fig. 5.14 (e) EDS spectrum of ARH
Fig. 5.14 (f) Elements present in CRH (weight %) from EDS analysis
5.3. EFFECT OF TEMPERATURE ON THE NANO-CRYSTALLINE SILICA AND CARBON COMPOSITES OBTAINED FROM RICE-HUSK ASH

5.3.1 Introduction:

Ultrafine silica powder finds potential applications in many industrially important products. Silica is an important ingredient of high-surface-area catalysts, sorption media, glass and cement manufacturing and dehydration systems [20]. This silica can be synthesized using complicated chemical routes [21, 22]. The rice husk, coming out of rice mills as a cheap by-product, offers a great opportunity for silica production more conveniently and at reduced expenses. At present, nano-silica materials are prepared using several methods, including vapor-phase reaction, sol-gel and thermal decomposition technique. The powder production of silica is a highly energy-intensive process. Unlike this, economically viable and high-grade, nano-size amorphous silica from rice husk can be produced simply by burning under appropriate conditions [23]. The major constituents of rice husk are hydrated silicon and organic materials consisting of cellulose (55–60 wt%, including cellulose and hemicelluloses) and lignin (22 wt %) [24]. The main advantage of producing silica in this manner is the highly-reactive nature of silica particles, requiring minimum grinding. The energy for burning is mostly supplied from the carbonaceous part of husk itself. Therefore, attempts by many workers have been made to produce silica from rice husk. Silica having large surface area and high porosity by burning rice husk has been produced [25]. During the process, about 20% mass of rice husk remains as ash, this contains 95 wt% of silica. It was found that leaching of rice husk with HCl at 75°C for 1 h prior to combustion produces amorphous silica of complete white color [26]. Nano-structured silica powders with high specific surface area have been obtained from non-isothermal decomposition of rice husk in an air atmosphere [7]. Effect of temperature on phase transitions of nano-crystalline silica obtained from rice husk has already been reported [27]. Furthermore, charring of rice husk produces nanosize silica-carbon-intermixed composite, which may find newer applications because such a product is not available synthetically. This may directly be converted to silicon carbide and silicon nitride at high temperature [16, 28]. The present section deals with the preparation of nano-crystalline silica and carbon composite powder obtained from the pyrolysis
of carbon-enriched rice husk ash (RHA), and the study of different phases of silica so formed is
done by X-ray diffractometer (XRD) analysis. The phase transformations of silica with respect to
temperature and carbon have also been studied from XRD plots. The crystallite sizes were
determined and a quantitative estimation was done from XRD plot. FT-IR was carried out to
confirm the presence of silica and carbon. Microstructural analysis was carried out to show the
presence of ultrafine particles.

5.3.2 Experimental details:

About 5 g samples of BA were taken in cylindrical alumina crucibles and introduced into a
muffle furnace for pyrolysis at different temperatures varying from 400°C to 1200°C at an
interval of 200°C for 2 h soaking time in static air. The pyrolysed products were analyzed by
XRD. A Philips XRD (Model PW 1830) with CuKα radiation through Ni filter was used.
Scanning electron microscopy (SEM) (JSM-6480 LV, JEOL) was used to study the surface
morphology of the charred products. FT-IR (Perkin Elmer, Model Spectrum RX1) analysis of the
pellet (using KBr press) samples was carried out to confirm the different bonds of Si/O system in
charred BA.

5.3.3 Results and discussion:

Fig.5.15 shows the composite XRD plot of pyrolysed BA at different temperatures (400–
1200°C). In this plot, mainly different phases of silica and graphite peaks can be observed. α-
quartz can be observed at 2θ ~ 21° till 800°C. A phase transformation of silica can be observed
from 1000°C to 1200°C. Another silica peak at 2θ ~ 26° shows the existence of both carbon and
silica. The peak at 2θ ~ 26° mainly shows carbon at 400°C and carbon and silica composite at
600°C. From temperature 800°C onwards, carbon cannot be detected at 2θ ~ 26°, instead a peak
of silica can be observed. Usually, carbon gets oxidized at 700°C in the presence of air [27].
With increase in temperature (i.e., at 1000°C), this peak becomes sharper, which may be due to
the fact that with increase in temperature, the crystallite size increases. At 1200°C, two major
peaks of silica can be observed. A distinct change of silica phase can also be detected. α-quartz
gets transformed into β-cristobalite, and the peak is shifted from 2θ ~ 21° to 2θ ~ 22° (Fig.5.15).
Crystallite size was calculated from the XRD graph by using Scherrer's equation (Eq. 1) [14]. The crystallite sizes were found to be 243.9Å – 672.7Å and are listed in Table 5.3.

![XRD analysis of BA charred at different temperatures (400 - 1200°C)](image)

Fig. 5.15 XRD analysis of BA charred at different temperatures (400 - 1200°C)

Table 5.3 Crystallite size of SiO₂ (hkl) and Carbon (hkl) in nm of black ash charred at different temperatures (400°C - 1200°C)

<table>
<thead>
<tr>
<th>Temperature in (°C)</th>
<th>Crystallite Size in °Å (hkl)</th>
<th>Identified Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>243.9 (002)</td>
<td>C</td>
</tr>
<tr>
<td>600</td>
<td>338.8 (111), (002)</td>
<td>SiO₂, C</td>
</tr>
<tr>
<td>800</td>
<td>446.8 (111)</td>
<td>SiO₂</td>
</tr>
<tr>
<td>1000</td>
<td>672.7 (111)</td>
<td>SiO₂</td>
</tr>
<tr>
<td>1200</td>
<td>414.7 (111)</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

The crystallite sizes increase gradually with increase in temperature from 400°C to 1000°C. This is because of the heat-induced expansion of crystallite size by reduction of crystallite thickness.
and agglomeration of small crystallites. The crystallite size observed here is quite large as compared to our earlier report (Ref. [27]). This may be due to extra heat absorbed by the sample during: (a) charring for preparation of BA (which was absent in earlier case), and (b) high heating rate (200°C for 2 h soaking time, which is almost twice that of the earlier heating rate) of the sample. At 1200°C, the phase change takes place and two major peaks of silica at 2θ ≈ 22° and 20 ≈ 26° can be detected. The crystallite sizes of these two peaks also get reduced to 414.7Å (at 2θ ≈ 26°) and 513.9Å (at 2θ ≈ 22°). From the XRD plot, it can be clearly observed that both the carbon and silica phases are present at 600°C. So, scanning electron micrographs of calcined BA at 600°C were done, and are shown in Fig.5.16 (a), to study the surface morphology. The physical appearance of the BA charred at 600°C in air, as shown in Fig.5.16 (a), is comparatively white in color with respect to BA (Fig.5.7), which may be due to the oxidation of carbon. From the morphology, we also find that it is difficult to distinguish between silica and carbon. This may be due to the fact that silica is in intimate contact with carbon. This is also confirmed from the XRD results. A higher magnification SEM of the BA sample calcined at 600°C in air has also been done to observe the particle size (Fig.5.16 (b)). The submicron particles are mainly cubical in nature. Some agglomerated particles along with very few whiskers can also be observed. The particle size ranges from 0.1μm to 1μm. Results obtained from the FT-IR spectroscopy of BA charred at 600°C are shown in Fig.5.17. As can be seen, RRH contains several absorption bands (Fig. 5.5), which have been assigned to individual structural units as listed in Table 5.2. The indication of dehydration is confirmed by the negligible intensity of the O-H stretching band (3600-3100 cm⁻¹) in BA (Fig.5.8) and BA charred in air when compared with that in RRH. Organic decomposition can be observed from the absence of a 2900 cm⁻¹ band representing C-H absorption, and peaks of CH₂ and CH₃ at 1500-1200 cm⁻¹ dramatically diminished. In BA charred in air, the band from 1600 cm⁻¹ may be due to aromatic C=C vibrations by neighbouring oxygen groups [19], and 1500 cm⁻¹ band may be due to C-H deformation. Improvement in aliphatic C-H deformation band indicates the enhancement of carbon contents of the composite powder because of the charring of BA at 600°C. The band from 1050 cm⁻¹ to 1100 cm⁻¹ corresponds to the Si-O bond vibration mode, which became sharper as the organic matter was pyrolysed.
Fig. 5.16 (a) Micrograph of charred BA at 600°C

Fig. 5.16 (b) High-resolution micrograph of charred BA at 600°C
5.4 EFFECT OF TEMPERATURE ON Si-BASED CERAMIC MATERIALS SYNTHESIZED FROM RICE HUSK

5.4.1 Introduction

Very high surface area and intimate contact available for the carbon and silica mixture can be obtained by heating rice husks (RHs) in a non-oxygen atmosphere. So, pyrolysed rice husk can provide the source of both carbon and silica. Simultaneously, because of the uniform distribution between carbon and silica in the rice husk, the reaction can occur more easily than in the case of conventional mechanical mixing technique. Due to these reasons, RHs are now-a-days recognized as a rich and abundant source for the preparation of Si-based ceramics of technological interest, viz. SiC, Si_3N_4, Si_3N_4 and high-purity silica [29-34]. Si-based, non-oxide ceramics made of Si compounds (SiC, Si_2N_2O and Si_3N_4) are advanced ceramic materials. Due to their high-temperature strength retention, thermal-stress resistance coupled with light weight, these compounds are found suitable for structural applications at high temperatures in chemical and material engineering. Previously, many works have been reported about the production of SiC and Si_3N_4 individually from rice husks, either in inert atmosphere, or in the presence of N_2 or NH_3 [35-37]. But very few works were reported on the composites of all these Si-based ceramics produced from RHs [34, 38-40]. Padhi and Patnaik had produced SiC, Si_3N_4 and Si_2N_2O in the presence of NH_3 from rice husk within the temperature range 1300 - 1600°C. The products were confirmed by XRD and IR analysis. Freitas et al. have confirmed the presence of SiC, Si_3N_4 and Si_2N_2O from RHs in N_2 and Ar atmosphere within the temperature range 1450 - 1700°C. XRD and NMR analysis was done to confirm the products. Role of catalysts in the formation of Si-based ceramics from RHs has already been reported in previous works [28, 41-42]. In the present work, an attempt has been made to produce Si-based ceramics in the absence of catalyst at a comparatively lower temperature (1100 - 1500°C) in N_2 atmosphere. The products have been characterized through XRD, FT-IR and EDS analysis to confirm the presence of SiC, Si_3N_4 and Si_2N_2O. SEM analysis was carried out to study the morphology of the products. Crystallite sizes of different phases were determined by using Scherer’s equation [14].
5.4.2 Experimental

The rice husks (RHs) used for this study were collected from a local rice mill of Rourkela (Odisha, India). The natural RHs were washed thoroughly with tap water followed by distilled water to remove the dirt and soil adhered on the husk and then dried in air. After that, precoking of this dried husks was carried out at the temperature of 700°C for 2 h under N$_2$ flow in order to remove the volatile materials, giving rise to a highly-carbonaceous material (named black ash, BA) used as precursor [41] for further heat treatment at higher temperatures. These final heat treatments were performed at 1100, 1300 and 1500°C under N$_2$ atmosphere (IOLAR-1), flow rate 190 ml/min, at the heating rate of 5°C/min for 1h in a tubular furnace. After the heat treatment was over, the gas flow was stopped.

Phase identification of the products was carried out by X-ray diffraction technique using a Philips (Model PW1830) diffractometer, fitted with a Cu cathode and Ni-filter at a scan rate of 2°/min. The crystallite sizes of different samples were calculated using Scherer's equation. The morphology of the product was studied by scanning electron microscope (JEOL, Model JSM-6480 LV), which was equipped with an EDS analysis facility. FT-IR (Perkin Elmer, Model spectrum RX1) analysis of the pallet samples (using KBr press) was carried out to confirm the different bonds of Si/C/N/O system.

5.4.3 Results and discussion

The carbothermal reduction reaction of silica to form SiC, Si$_3$N$_4$ and Si$_2$N$_2$O can be written as

$$\text{SiO}_2(s) + 3\text{C}(s) \rightarrow \text{SiC}(s) + 2\text{CO} \text{ (g)} \quad \ldots (1)$$

$$3\text{SiO}_2(s) + 6\text{C}(s) + \frac{3}{2}\text{N}_2 \text{(g)} \rightarrow \text{Si}_3\text{N}_4(s) + 6\text{CO} \text{(g)} \quad \ldots (2)$$

$$2\text{SiO}_2 \text{(g)} + \text{N}_2 \text{(g)} + 3\text{C}(s) \rightarrow \text{Si}_2\text{N}_2\text{O}(s) + 3\text{CO} \text{(g)}. \quad \ldots (3)$$

From the above reactions and the chemical analysis as reported earlier [41], it can be found that C/SiO$_2$ weight ratio of the rice husk material is higher than the required weight ratio for the formation of SiC, Si$_3$N$_4$ and Si$_2$N$_2$O.
The X-ray diffraction patterns of heat-treated BA at different temperatures (1100°C, 1300°C and 1500°C) with soaking time 1h in an N₂ atmosphere (IOLAR-1) are shown in Fig.5.17. Detailed XRD data of different phases are listed in Table-5.4. At 1100°C, the XRD pattern exhibits the peaks with very small intensity at 2θ ~ 22° and 26°. A hump can also be observed near this region. This evidences the presence of silica and carbon [27]. At pyrolysis temperature 1300°C, peaks of SiC (2θ ~ 36°) and Si₂N₂O (2θ ~ 26°) can be detected along with crystalline phase of SiO₂ (cristobalite). As per Padhi and Patnaik [38], SiO₂ and C react to form SiO and CO. So, this indicates that reaction between SiO₂ and C has not started at 1100°C. But as the temperature increased to 1300°C, the reaction between SiO₂ and C has started to form SiO and CO. So, formation of SiC and Si₂N₂O can be detected. A large intense peak at 2θ ~ 22° shows that a good amount of SiO₂ remained unreacted. This may be due to the formation of SiO. The atmosphere of SiO around SiO₂ doesn’t allow SiO₂ to react further with C/CO. At 1500°C, SiO₂ peaks become more intense due to increase in temperature. Si₂N₂O can be observed with higher peak at 2θ ~ 26°. Peak of Si₃N₄ along with SiC can be observed near 2θ ~ 36°. As reported by Freitas et al. Si₃N₄ can be observed at 1450°C with higher heating rate. In another work, Kumar and Godkhindi [34] has reported the presence of Si₂N₂O and SiC along with cristobalite at 1350°C by incorporating Si- additive. No Si₃N₄ phase can be detected. The reasons mentioned were as follows:

1) Lower flow rate of N₂ 50 ml/min, and
2) CO gas is not effectively removed from the system as the cap of the holder is closed.

In the present experiment, flow rate of N₂ was increased to 190 ml/min and the samples were placed in a graphite boat and remained open so that N₂ can enter into the sample holder easily and CO can be removed. So, this may cause the formation of Si₃N₄ along with two other phases SiC and Si₂N₂O. The crystallite sizes were calculated using Scherer’s equation and tabulated in Table-5.4. The crystallite size of silica decreases from 1100°C to 1300°C, which may be due to the different phase transformation. After that, it remains the same till 1500°C. The crystallite size of Si₂N₂O increases from 1100 to 1300°C, again decreases at 1500°C, which may be due to different phase formation. No SiC peak can be observed at 1100°C. The formation starts from 1300°C and the crystallite size increases with temperature, which may be due to agglomeration. The formation of Si₃N₄ was observed only at 1500°C. The crystallite sizes of all the ceramics lie within the range 265.5Å - 821.6Å.
Fig. 5.17. XRD analysis of BA pyrolysed at different temperatures (1100°C - 1500°C) in N₂/1h

Fig. 5.18 shows the scanning electron micrographs of the samples fired at 1100°C, 1300°C and 1500°C in N₂ atm. /h. The sample fired at 1100°C, Fig. 5.18 (a), appears to retain the original form of the charred rice husk. SiO₂ and C can't be detected separately because both of them are mainly in amorphous form and in intimate contact with each other at their molecular level [43]. A few white colored particles can be observed, which may be due to the formation of α-quartz, as confirmed from XRD. Visual inspection shows that the colour of the sample fired at 1100°C appears to be black. A remarkable change can be noticed after firing the sample at 1300°C. Most of the black ash has changed its shape and size. It appeared to be more uniformly distributed, as shown in Fig. 5.18 (b). So, most of the black ash has taken part in the reaction and changed into various phases like cristobalite, SiC, Si₂N₂O, etc. as confirmed from XRD. The visual effect of the sample fired at 1300°C appears to be grey in colour. A noticeable change can be observed for the sample fired at 1500°C (Fig. 5.18(c)) in comparison to the samples fired at 1100°C and
1300°C. No rice husk in its original form can be observed here. Almost all the husk has taken part in the reaction and is uniformly distributed. The Si₃N₄ phase can be observed here along with cristobalite, SiC and Si₂N₂O as confirmed from XRD. The visual inspection shows that the sample fired at 1500°C appears to be greenish in colour. As maximum number of Si-based ceramics phases was observed at 1500°C, so, the EDS analysis of the same sample was done (Fig.5.19), confirming the presence of Si, N, C and O.

Fig. 5.18(a) SEM of BA calcined at 1100°C in N₂/1h

Fig. 5.18(b) SEM of BA calcined at 1300°C in N₂/1h
Fig. 5.18(c) SEM of BA calcined at 1500°C in N₂/1h

Fig. 5.19 EDS analysis of BA calcined at 1500°C in N₂/1h
FT-IR analysis, from Fig. 5.20 (a), confirms the presence of Si and O bonding at 1091 cm\(^{-1}\). The absorption band near 2350 cm\(^{-1}\) confirms the presence of C\(=\)N [44]. The peak near 790 cm\(^{-1}\) indicates the presence of Si and C bonding. The presence of the peak near 460 cm\(^{-1}\) may be due to Si-O bonding [38].
Fig. 5.20 (b) FT-IR analysis of BA pyrolysed at 1300°C/N\textsubscript{2}/1h. The absorption bands near 2350 cm\textsuperscript{-1}, 1091 cm\textsuperscript{-1} resemble with those of Fig.5.20 (a) and show the presence of C=N and Si-O bonding. Peaks at 790 cm\textsuperscript{-1} confirm Si-C bonding. Here, peaks at 470 cm\textsuperscript{-1} and 621 cm\textsuperscript{-1} may be due to the presence of Si-N bonding. In Fig. 5.20 (c), sample pyrolyzed at 1500°C shows almost the same peaks as in the case of Fig.5.20 (b). Only the intensity of the SiO\textsubscript{2} at 1091 cm\textsuperscript{-1} peak becomes smaller and narrower. This may be due to the phase transformation or increase in crystallinity with increase in temperature. From XRD analysis (Fig.5.17), the peak at \approx 26° matches with Si\textsubscript{2}N\textsubscript{2}O peaks along with C peak at 1100°C. But from FT-IR analysis, no Si-N bonding can be observed at 1100°C. Hence, it can be concluded that chances of formation of Si\textsubscript{2}N\textsubscript{2}O is very less at 1100°C. But it started from 1300°C onwards as confirmed both from XRD and FT-IR analysis.
Fig. 5.20 (c) FT-IR analysis of BA pyrolysed at 1500°C/N₂/1h
Table-5.4 X-ray diffraction data for the phase analysis of BA charred in N$_2$/II$_1$ as a function of temperature

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>2θ (deg.)</th>
<th>Interplanar spacing ‘d’(Å)</th>
<th>Intensity (cps)</th>
<th>h k l</th>
<th>Full Width Half Maxima ‘FWHM’ (deg.)</th>
<th>Crystallite Size (Å)</th>
<th>Identified Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>20.920</td>
<td>4.2428</td>
<td>458</td>
<td>100</td>
<td>0.0984</td>
<td>821.6</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>26.695</td>
<td>3.3366</td>
<td>1656</td>
<td>101</td>
<td>0.1771</td>
<td>461.2</td>
<td>Si$_3$N$_2$O, SiO$_2$</td>
</tr>
<tr>
<td>1300</td>
<td>21.865</td>
<td>4.0615</td>
<td>2088</td>
<td>101</td>
<td>0.2165</td>
<td>373.7</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>26.525</td>
<td>3.3576</td>
<td>683</td>
<td>111</td>
<td>0.1181</td>
<td>691.4</td>
<td>Si$_3$N$_2$O, SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>35.9736</td>
<td>2.4966</td>
<td>252</td>
<td>100</td>
<td>0.3149</td>
<td>265.5</td>
<td>SiC</td>
</tr>
<tr>
<td>1500</td>
<td>21.915</td>
<td>4.0524</td>
<td>4692</td>
<td>101</td>
<td>0.2165</td>
<td>373.7</td>
<td>SiO$_2$</td>
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<td>26.495</td>
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<td>4134</td>
<td>111</td>
<td>0.1378</td>
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<td>100</td>
<td>0.1574</td>
<td>530.3</td>
<td>SiC</td>
</tr>
<tr>
<td></td>
<td>36.035</td>
<td>2.4903</td>
<td>640</td>
<td>210</td>
<td>0.1574</td>
<td>530.7</td>
<td>Si$_3$N$_4$</td>
</tr>
</tbody>
</table>
5.5 EFFECT OF AN IRON CATALYST AND PROCESS PARAMETERS ON SI-BASED CERAMIC MATERIALS SYNTHESIZED FROM RICE-HUSK

5.5.1 Introduction:

In recent years, ceramic-matrix or metal-matrix composites have become of great interest because of their high-temperature strength retention as well as thermal-stress resistance coupled with their light weight. As a consequence, different types of Si-based ceramic materials such as SiC, Si₃N₄ and Si₂N₂O are available commercially [33, 6]. For the production of SiC, Si₃N₄ and Si₂N₂O, both the important raw materials SiO₂ and carbon are present in RH with intimate contact and they possess a high surface area. Therefore, it is not surprising that, due to the ease of further processing, RH was reported to be used in the production of SiC, Si₃N₄ and Si₂N₂O by several authors [38, 39, and 45]. SiC whiskers, useful in reinforcing the metal-matrix and ceramic-matrix composites, are already reported to be produced using RH [29, 46, 47]. The synthesis of Si₃N₄ and the effect of seeding with α-Si₃N₄ on the formation of α-Si₃N₄ from SiO₂ and carbon mixture [48] and from rice husk [49] have already been studied. In another study, the behavior of silica during the formation of Si₃N₄ by carbothermal route has been investigated [50]. Silicon nitride-silicon carbide composite powders with mean diameter about less than 700 nm useful for preparing sintered ceramic bodies and self-reinforced silicon nitride ceramic bodies have been reported to be produced [51]. In the present work, the effect of an iron catalyst on the formation of Si₃N₄ along with Si₂N₂O and SiC material in a N₂ atmosphere was studied. An attempt was also made to study the effect of temperature and concentration of the Fe catalyst on the formation of the product material. X-ray diffraction (XRD), energy dispersive X-ray (EDX) spectroscopy and Fourier-transform-infra-red (FT-IR) spectroscopy analyses were performed to confirm the presence of SiC, Si₃N₄ and Si₂N₂O. The formation of whiskers, particles and surface morphology has been studied through scanning electron microscopy (SEM).
5.5.2 Experimental Details:

The charred rice husk, named black ash (BA), was treated with HCl (1:1), followed by washing thoroughly with distilled water, and dried in air. Subsequently, Fe in its sulphate form with various concentrations (4–10%) was impregnated as follows: FeSO₄ salt (4%, 6%, 8% and 10% Fe) was dissolved in 100 ml distilled water by stirring. About 5 g of black ash was added in each beaker and soaked for 1 h. Excess FeSO₄ solution was removed. The FeSO₄-soaked black ash was then treated with 10% NH₃ solution with holding time of 1 h for precipitation of Fe(OH)₃. Excess NH₃ solution was removed. The iron-impregnated black ash was then washed with distilled water thoroughly and dried in air for 24 h. From the literature [42], 5% Fe concentration in SiO₂: C mixture for SiC formation has been found to be suitable. Therefore, the concentration of Fe was chosen from less than and above 5% (i.e.; 4–10%) to study the effects on the products. These Fe-impregnated rice husks (4–10%) were taken in a graphite crucible, placed in a tubular furnace and heat-treated at 1400°C in N₂ atmosphere (IOLAR 1) at the rate of 5°C/min for 1 h. After the heat treatment was over, the gas flow was stopped. Phase identification of the products was carried out by X-ray diffraction technique using a Phillips (Model PW1830) diffractometer, fitted with a Cu cathode and Ni-filter, at a scan rate of 2°/min. The presence of different phases such as SiC, Si₃N₄, Si₂N₂O, unreacted SiO₂ and carbon was detected. FT-IR (Perkin Elmer, Model Spectrum RX1) analysis of the pallet samples (using KBr press) was carried out to confirm the different bonds of Si/C/N/O system. The morphology of the product was studied by scanning electron microscope (JEOL, Model JSM-6480 LV), which was equipped with an EDX analysis facility.

BA + Fe (8%) fired at 1400°C/1 h/N₂ shows both SiC and Si₃N₄. It also contains both particles and whiskers of comparable amounts. So also does the BA + Fe (8%) sample fired at different temperatures (1200°C, 1300°C and 1450°C) with 1 h holding time in the same N₂ atmosphere. The XRD analysis was carried out to show the different phases. The morphology of the product was studied by scanning electron microscope.

5.5.3 Results and Discussion:

The carbothermal reduction reaction of silica to form SiC, Si₃N₄ and Si₂N₂O can be written as

\[ \text{SiO}_2 (s) + 3\text{C} (s) \rightarrow \text{SiC} (s) + 2\text{CO} (g) \]  

... (1)
Fig. 5.21 XRD patterns of BA+ Fe with different concentrations fired at 1400°C/1 h/N₂

The X-ray diffraction patterns of Fe-impregnated black ash (BA) with different concentrations fired at 1400°C/1 h in a N₂ atmosphere (IOLAR-1) are shown in Fig. 5.21.
Table-5.5 X-ray diffraction data for phase analysis as a function of catalyst concentration (%)

<table>
<thead>
<tr>
<th>Catalyst (%)</th>
<th>2θ (deg.)</th>
<th>Interplanar spacing 'd' (Å)</th>
<th>Intensity (cps)</th>
<th>h k l</th>
<th>Full Width Half Maxima 'FWHM' (deg.)</th>
<th>Crystallite Size (Å)</th>
<th>Identified Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>21.96</td>
<td>4.04</td>
<td>187.45</td>
<td>101</td>
<td>0.3149</td>
<td>257.04</td>
<td>SiO₂</td>
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<tr>
<td>26.67</td>
<td>3.34</td>
<td>892.10</td>
<td>111, 002</td>
<td></td>
<td>0.1181</td>
<td>690.76</td>
<td>SiO₂, C</td>
</tr>
<tr>
<td>35.80</td>
<td>2.50</td>
<td>456.88</td>
<td>111</td>
<td></td>
<td>0.0984</td>
<td>848.85</td>
<td>SiC</td>
</tr>
<tr>
<td>6</td>
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<td>4.04</td>
<td>3332.78</td>
<td>101</td>
<td>0.1968</td>
<td>411.28</td>
<td>SiO₂</td>
</tr>
<tr>
<td>26.73</td>
<td>3.33</td>
<td>2303.69</td>
<td>111, 002</td>
<td></td>
<td>0.0984</td>
<td>830.17</td>
<td>Si₂N₂O₃, C</td>
</tr>
<tr>
<td>28.47</td>
<td>3.13</td>
<td>218.47</td>
<td>110</td>
<td></td>
<td>0.1574</td>
<td>520.99</td>
<td>Fe-Si</td>
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<tr>
<td>36.64</td>
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<td>0.1181</td>
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<td>8</td>
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<td>0.1771</td>
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<td>SiO₂</td>
</tr>
<tr>
<td>26.50</td>
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<td>628.66</td>
<td>111, 002</td>
<td></td>
<td>0.0984</td>
<td>830.22</td>
<td>Si₂N₂O₃, C</td>
</tr>
<tr>
<td>28.47</td>
<td>3.13</td>
<td>140.22</td>
<td>110</td>
<td></td>
<td>0.1574</td>
<td>520.99</td>
<td>Fe-Si</td>
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<td>35.68</td>
<td>2.51</td>
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<td>111, 210</td>
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<td>0.1574</td>
<td>530.39</td>
<td>SiC, Si₃N₄</td>
</tr>
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<td>659.97</td>
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<td>1037.23</td>
<td>Si₂N₂O₃, C</td>
</tr>
<tr>
<td>28.25</td>
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<td>Fe-Si</td>
</tr>
<tr>
<td>35.98</td>
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<td>210</td>
<td></td>
<td>0.1574</td>
<td>530.74</td>
<td>Si₃N₄</td>
</tr>
</tbody>
</table>

Detailed XRD data of different phases are listed in Table 5.5. XRD analysis of the above products shows that maximum numbers of phases are present in 8% Fe-impregnated husk charred at 1400°C. Hence, 8% concentration was chosen to further study the effect of temperature and elemental analysis (EDX). The heat treatments were carried out with different temperatures 1200, 1300, 1400 and 1450°C for the 8% Fe-impregnated husk with 1 h soaking time. Peaks of unreacted silica and carbon can be seen for all the cases. The degree of crystallization of silica increases with increase in Fe concentration, but carbon crystallization decreases. At 4% Fe loading, the formation of SiC (JCPDS file no.29-1129) peak is more intense than for the 6% and 8% Fe concentration.
A new intermetallic phase Fe-Si (JCPDS file no.01-1271) can be observed from 6% Fe concentration onwards. It is observed that the Fe-Si peak decreases with increase in Fe concentration. A shift in the peak position with higher Fe concentration is also observed. From 6% Fe concentration, the carbon peak at 2θ=26.4° (JCPDS file no.26-1080), became smaller and the peak also matched with Si$_3$N$_2$O (JCPDS file no.83-2147). From 8% Fe concentration, a peak of Si$_3$N$_4$ was obtained (JCPDS file no.29-1132) at 2θ=36°. Another small peak can also be observed near 2θ=34° for the same concentration. This peak was detected as a compound of Fe$_2$(SiO$_4$)$_3$. At 8% Fe concentration, SiC peak has higher intensity than Si$_3$N$_4$. At 10% Fe concentration, Si$_3$N$_4$ became more prominent. From Table 5.5, it can be observed that, the crystallite size of Fe-Si and SiC and Si$_3$N$_4$ peak decrease gradually with an increase in Fe catalyst %. This may be due to the lattice strain developed for the excess amount of Fe present in the compound. The effect of Fe as a catalyst towards the formation of SiC, Si$_2$N$_2$O and Si$_3$N$_4$ phase can be observed after the formation of the Fe-Si intermetallic phase. At lower concentration (4%), no Fe-Si phase can be detected. SiO$_2$ and C being the dominating phases, they get reacted to produce SiC. As the concentration of Fe (6%) increased, an intermetallic phase Fe-Si can be observed. So, the nitridation of SiO$_2$ and carbon becomes possible, thus forming Si$_2$N$_2$O and Si$_3$N$_4$ [42].

Microstructural analyses of the samples were performed via SEM. The Fig.5.22 (a)-(d) shows the SEM of BA impregnated with different concentrations of Fe (4—10%) fired at 1400°C/1 h/N$_2$. The formation of whiskers of the product started at BA+ Fe (4%). As the concentration increased to 6%, the quantity of whisker formation also increased. With further increase in Fe concentration, as shown in Fig. 5.22(c) and (d), a lower quantity of whiskers and higher quantity of particulates were observed. The role of iron catalyst in the reaction mechanism of the formation of silicon carbide and silicon nitride were explained clearly by Siddiqi [52]. The Fe-Si liquid phase accelerates the reaction mechanism. This liquid phase will act as a sink for silicon (from SiO reaction), carbon and a source of SiC and Si$_3$N$_4$ precipitation. As reported by Janghorban et al. [53], the nucleation of the SiC whiskers was found to occur at sites of the impurities and grew outwards, which indicated that Si from peak areas diffused via a gas phase to combine with the cellulose containing carbon at the valleys to form SiC. Therefore, more precipitation of SiC, Si$_3$N$_4$ took place and the products gradually turned to globules from whiskers with increase in Fe concentration. As the maximum number of phases was found in the
8% impregnated sample, an EDX analysis was performed for this sample as shown in Fig. 5.23. The figure confirms the presence of Si, C, N and O.

Fig. 5.22 SEM micrographs of BA+Fe samples: a) 4% Fe, b) 6% Fe, c) 8% Fe, d) 10% Fe; fired at 1400°C/1h/N₂
Results obtained from the FTIR spectroscopy experiments performed on the BA+ Fe (4 – 10%) pyrolysed at 1400°C/1 h/N2 are shown in Fig. 5.24. The absorption band near 2400 cm⁻¹ was attributed to the presence of C=N [44]. The peak at approximately 1099 cm⁻¹ has become broad. This is due to the Si and O bonding, matching with the XRD results, which confirms the presence of cristobalite or quartz silica [6]. Absorption bands at 1600 cm⁻¹ may be due to aromatic C=C skeletal vibration and C-C/C-O skeletal vibrations, respectively, which may have appeared due to the incomplete decomposition of organic compounds [54]. The peak at 790 cm⁻¹ indicates the presence of SiC [6]. The peaks at 493 and 684 cm⁻¹ show the bonding of Si-N. BA+ Fe (8%) fired at 1400°C/1 h/N2 shows both SiC and Si₃N₄. It also contains both particles and whiskers of comparable amounts.
The BA+ Fe (8%) samples were fired at different temperatures (1200°C, 1300°C and 1450°C) with 1 h holding time in the same N₂ atmosphere. The XRD patterns of the above samples are shown in Fig. 5.25. Silica peaks (2θ=22°) became sharper with the rise in temperature. Intensity of carbon/Si₂N₂O (2θ = 26°) decreases with a rise in temperature. At lower temperature (1200°C), only the silicon nitride peak can be observed (2θ=36°). As the temperature increased to 1300°C, another peak of SiC also appeared. At 1450°C, only the SiC peak with comparatively higher intensity can be observed. It can be noted that the peak at (2θ ≈ 28°) changes from silica (at temperature 1300°C) to Fe-Si (at temperature 1450°C). An intermetallic phase of Fe-Si exists above 1300°C, which has been reported elsewhere [52]. Below this temperature, no liquid phase was observed, confirming the non-occurrence of the SiC phase.
SEM of the 8% Fe doped rice husks fired at different temperatures i.e. a) 1200°C, b) 1300°C, and c) 1450°C, are shown in Fig. 5.26 (a) – (c). At 1200°C [Fig.5.26 (a)], the two major phases SiO$_2$ and carbon can be observed in the form of globules. As the temperature increased to 1300°C [Fig.5.26 (b)], the particulates started melting, which may be due to the formation of Fe-Si intermetallic phase. This result also matches well with the XRD result [Fig.5.25]. With the increase in temperature, i.e. at 1400°C [Fig. 5.22 (c)], formations of fine whiskers can be observed. It can also be observed that the beading up of whiskers to particles was started at this stage. With further increase in temperature, i.e. at 1450°C [Fig. 5.26 (c)], formations of uniform spherical shaped particles have appeared. The iron-silicon phase diagram contains four eutectics.
Fig. 5.26 SEM micrographs of BA+Fe (8%) fired at a) 1200°C b) 1300°C c) 1450°C for 1h in N$_2$ atmosphere.
at around 1250°C [55] and the formation of Fe-Si liquid phase at the reaction temperature is therefore possible. In contact with excess carbon, this liquid phase will be saturated with carbon. So, the precipitation of SiC or Si$_3$N$_4$ will start in the form of particles.
5.6 EFFECT OF AN NICKEL CATALYST AND PROCESS PARAMETERS ON SI-BASED CERAMIC MATERIALS SYNTHESIZED FROM RICE-HUSK

5.6.1 Introduction:

The effect of Ni catalyst on the production of SiC from rice husk has already been reported earlier [28, 42]. In the present work, the effect of Ni catalyst on the formation of Si$_3$N$_4$ along with Si$_2$N$_2$O and SiC material in an N$_2$ atmosphere has been studied. An attempt has also been made to study the effect of temperature and concentration of the Ni catalyst on the formation of the product material. X-ray diffraction (XRD), energy dispersive X-ray (EDX) spectroscopy and Fourier transform-infra red (FTIR) spectroscopy analyses were performed to confirm the presence of SiC, Si$_3$N$_4$ and Si$_2$N$_2$O. The formations of whiskers, particles and surface morphology have been studied through Scanning Electron Microscopy (SEM).

5.6.2 Experimental Details:

The charred rice husk, named black ash (BA), was treated with HCl (1:1), followed by washing thoroughly with distilled water, and dried in air. Subsequently, Ni in its sulphate form with various concentrations (2–10%) was impregnated as follows: NiSO$_4$ salt (2%, 6% and 10% Ni) was dissolved in 100 ml distilled water by stirring. About 5 g of black ash was added in each beaker and soaked for 12 h. Excess NiSO$_4$ solution was removed. The iron-impregnated black ash was then washed with distilled water thoroughly and dried in air for 24 h. From the literature [42], 5% Ni concentration in SiO$_2$: C mixture for SiC formation has been found to be suitable. Therefore, the concentration of Ni was chosen from less than and above 5% (i.e.; 2–10%) to study the effect on the products. These Ni-impregnated rice husks (2–10%) were taken in a graphite crucible, placed in a tubular furnace and heat-treated at 1400°C in N$_2$ atmosphere (IOLAR 1) at the rate of 5°C/min for 1 h. After the heat treatment was over, the gas flow was stopped. Phase identification of the products was carried out by X-ray diffraction technique using a Philips (Model PW1830) diffractometer, fitted with a Cu cathode and Ni-filter, at a scan rate of 2°/min. The presence of different phases such as SiC, Si$_3$N$_4$, Si$_2$N$_2$O, unreacted SiO$_2$ and carbon was detected. FT-IR (Perkin Elmer, Model Spectrum RX1) analysis of the pallet samples (using KBr press) was carried out to confirm the different bonds of Si/C/N/O system. The morphology
of the product was studied by scanning electron microscope (JEOL, Model JSM-6480 LV), which was equipped with an EDX analysis facility.

5.6.3 Results and Discussion:

The X-ray diffraction patterns of Ni impregnated black ash (BA) with different concentrations fired at 1400°C/1 h in an N₂ atmosphere (IOLAR-1) are shown in Fig. 5.27. Detailed XRD data of different phases are listed in Table 5.6. XRD analysis of the above products shows that maximum numbers of phases are present in 10% Ni-impregnated husk charred at 1400°C. Hence, 10% concentration was chosen to further study the effect of temperature and elemental analysis (EDX). The heat treatments were carried out with different temperatures 1100, 1300 and 1400°C for 10% Ni-impregnated husk with 1 h soaking time (Fig.5.28). Peaks of unreacted silica and carbon can be seen for all the cases. At 2% Ni loading, the formation of SiC (JCPDS file no.29-1129) peak is more intense than that for the 6% and 10% Ni concentration (Fig.5.27).

A new intermetallic phase Ni₃Si₂ (JCPDS file no.03-1057) can be observed from 2% Ni concentration onwards. At 10% Ni concentration, another phase of NiSi can be observed may be due to higher concentration of Ni. From 6% Ni concentration, the carbon peak at 2θ=26.6° (JCPDS file no.42-1360) became smaller and the peak also matched with Si₃N₂O (JCPDS file no. 18-1171). At 6% Ni concentration onwards, a peak of Si₃N₄ was also observed (JCPDS file no.33-1160) at 2θ=36°. From Table 5.6, it can be observed that, the degree of crystallization of silica remains almost the same with increase in Ni concentration. The crystallite size of SiC peak remains almost the same with increase in Ni catalyst %. The crystallite size increases at 6% to 10% may be due to the formation of a new phase, i.e. Si₃N₄. The effect of Ni as a catalyst towards the formation of SiC, Si₃N₂O and Si₃N₄ phase can be observed after the formation of the Ni₃Si₂ intermetallic phase. At lower concentration (2%), SiO₂ and C being the dominating phases, get reacted to produce SiC. Si₂N₂O phase is also observed. As the concentration of Ni (6%) is increased, the nitridation of SiO₂ and carbon becomes more, thus forming Si₃N₄ [42].
To observe the effect of temperature towards the formation of various Si-based ceramic materials, 10% Ni-impregnated husk was chosen as maximum no. of phases were observed in it. The 10% Ni-impregnated husk was further heat treated at 1100°C and 1300°C along with 1400°C for 1h at N₂ atm. At 1100°C (from Fig. 5.28), silica in its quartz form (JCPDS file no. 03-0419) can be observed at 2θ=20.80°. Only graphite (JCPDS file no. 42-1360) with higher intensity can be observed at 2θ=26.6°. A small peak of SiC was also observed at 2θ=60°. No other phases such as Si₂N₂O or Si₃N₄ were observed at 1100°C. As the temperature rises to 1300°C, along with quartz, silica shows its cristobalite form (JCPDS file no. 11-0695). At 2θ=26.6°, a phase of Si₂N₂O can be observed along with graphite. The intermetallic phase Ni₂Si₂ or NiSi can be observed from 1300°C onwards. Formation of Si₃N₄ can be observed at 1400°C. No Si₃N₄ can be observed below 1400°C.
From Table 5.7, it can be observed that the crystallite size of silica decreases from 1100°C to 1300°C. This may be due to the formation of the new phase, i.e., cristobalite. After that, the crystallite size of cristobalite increases from 1300°C to 1400°C. The crystallite size of SiC decreases from 1100°C to 1300°C as there is a phase transformation. No Si$_3$N$_4$ peak can be observed till 1300°C.

Fig. 5.29 (a) to (c) shows the FTIR analysis of 2-10% Ni-doped BA fired at 1400°C/1h. In the Fig. 5.29 (a) to (c), the absorption bands near 1100 cm$^{-1}$ and 460 cm$^{-1}$ confirm the presence of Si-O bonding. The peak near 790 cm$^{-1}$ shows the presence of Si and C bonding. The absorption band near 650 cm$^{-1}$ shows the presence of Si-N bonding [35, 44]. The intensity of Si-O bonding is wider at 6% Ni-doped BA in Fig. 5.29 (b) than in Fig. 5.29 (a) (at 2% Ni doped BA). Again, it is narrower in Fig. 5.29 (c) (at 10% Ni doped BA). These changes may be due to the phase transformation of silica with change in Ni %. Other peaks are almost the same in all the cases, i.e., in Fig. 5.29 (a) to (c).
The Fig. 5.30 (a) and (b) shows the FTIR analysis of 10% Ni-doped BA charred at 1100°C/1h and 1300°C/1h, respectively. Almost the same peaks are observed in both the cases (i.e., in Fig 5.30 (a) and (b)) like 5.29 (c) (i.e. like 10% Ni -doped BA charred at 1400°C/1h). Only in case of Fig.5.30 (a), no Si-N bonding near 650 cm$^{-1}$ is observed showing the absence of Si$_3$N$_4$. The peak at 790 cm$^{-1}$ is also very small showing less intensity of Si-C bonding at 1100°C.

Fig. 5.31 (a) to (c) shows the SEM micrographs of BA+Ni samples (2% - 10% Ni) fired at 1400°C/1h/N$_2$. Fig. 5.31 (a) and (b) shows some agglomerated particles, some of which are white in color. The white-color intensity of the particles increases in 5.31 (b) than in 5.31 (a), which may be due to formations of more number of phases. Fig. 5.31 (c) shows the particles with different characteristics than the other two (i.e., Fig. 5.31(a) and (b)). In this case, the particles have started to become globules. A large number of tiny particles can be observed on the surface. As observed from the XRD analysis, maximum phases are observed in this case. So, it may be due to this reason that particles of various shape and sizes can be observed. Fig. 5.32 (a) and (b) shows SEM analysis of 10% Ni + BA treated at various temperatures (i.e., at 1100 and 1300°C/1h/N$_2$). At 1100°C, a few white colored particles are observed, showing the reaction has taken place due to charring. Other small particles of rice husk remains as it is. At 1300°C, it can be observed that, no. of white particles is more and particles are also comparatively larger than those of 1100°C. This may happen due to the increase in temperature. As maximum no. of phases can be observed at 1400°C for 10% Ni + BA, so the EDS analysis of this sample was carried out to confirm the presence of the elements Si, C, N and O.
Table 5.6 X-ray diffraction data for phase analysis as a function of Ni concentration (%)

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<th>Catalyst (%)</th>
<th>2θ (deg.)</th>
<th>Inter-planar spacing 'd'(Å)</th>
<th>Intensity (cps)</th>
<th>h k l</th>
<th>Full Width Half Maxima ‘FWHM’ (deg.)</th>
<th>Crystallite Size (Å)</th>
<th>Identified Phase(s)</th>
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<td>SiC, Si₃N₄</td>
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Table 5.7 X-ray diffraction data for phase analysis as a function of temperature

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<th>h k l</th>
<th>Full Width Half Maxima 'FWHM' (deg.)</th>
<th>Crystallite Size (Å)</th>
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<td>353.90</td>
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Fig. 5.29 (a) FT-IR analysis of 2% Ni doped BA fired at 1400°C

Fig. 5.29 (b) FT-IR analysis of 6% Ni doped BA fired at 1400°C
Fig. 5.29 (c) FT-IR analysis of 10% Ni doped BA fired at 1400°C

Fig. 5.30 (a) FT-IR analysis of 10% Ni doped BA fired at 1100°C
Fig. 5.30 (b) FT-IR analysis of 10% Ni doped BA fired at 1300°C
Fig. 5.31 SEM micrographs of BA+Ni samples: a) 2% Ni, b) 6% Ni, and c) 10% Ni fired at 1400°C/1h/N₂
Fig. 5.32 SEM micrographs of BA+Ni (10%) fired at: a) 1100°C, and b) 1300°C for 1h in N₂ atmosphere.

Fig. 5.33 EDS analysis of BA+Ni (10%) fired at 1400°C for 1h in N₂ atmosphere.
5.7 EFFECT OF SILICON ADDITIVES ON MAXIMIZATION OF WHISKERS FORMATION OF SI-BASED CERAMIC MATERIALS SYNTHESIZED FROM RICE-HUSK

5.7.1 Introduction:
The effect of Si additive on production of SiC and Si$_3$N$_4$O from rice husk has already been reported [34]. In the present work, the effect of Si additive on the formation of Si$_3$N$_4$ along with Si$_2$N$_2$O and SiC material in an N$_2$ atmosphere was studied. An attempt was also made to study the effect of the concentration of the Si additive on the formation of whiskers on the product material. X-ray Diffraction (XRD), Energy Dispersive X-ray (EDX) spectroscopy and Fourier Transform Infra Red (FTIR) spectroscopy analyses were performed to confirm the presence of SiC, Si$_3$N$_4$ and Si$_2$N$_2$O. The formations of whiskers and surface morphology have been studied through Scanning Electron Microscopy (SEM).

5.7.2 Experimental:
The charred rice husk, named as black ash (BA), was treated with HCl (1:1), followed by washing thoroughly with distilled water and dried in air. Subsequently, Si in its powder form with various concentrations (5–15%) by weight with respect to BA was added as follows. Si powder was weighed carefully in a physical balance and mixed thoroughly with BA in a plastic container with zirconia balls for 6 h. From the literature [34], till 5% Si concentration in SiO$_2$: C mixture for SiC formation, no remarkable change was found. Therefore, the concentration of Si was chosen from above 5% (i.e.; 5–10–15%) to study the effects on the products. These Si-added BA were taken in a graphite crucible, placed in a tubular furnace and heat treated at 1400°C in N$_2$ atmosphere (IOLAR 1) at the rate of 5°C/min for 1 h. After the heat treatment was over, the gas flow was stopped. Phase identification of the products was carried out by X-ray diffraction technique using a Phillips (model PW1830) diffractometer, fitted with a Cu cathode and Ni-filter, at a scan rate of 2°/min. The presence of different phases such as SiC, Si$_3$N$_4$, Si$_2$N$_2$O, unreacted SiO$_2$ and carbon were detected. FTIR (Perkin Elmer, model Spectrum RX1) analysis of the pallet (using KBr press) samples were carried out to confirm the different bonds of Si/C/N/O system. The morphology of the product was studied by scanning electron microscope (JEOL, model JSM-6480 LV), which was equipped with an EDX analysis facility.
5.7.3 Results and Discussion:

The X-ray diffraction patterns of Si-impregnated black ash (BA) with different concentrations fired at 1400°C/1 h in an N\textsubscript{2} atmosphere (IO-LAR-1) are shown in Fig. 5.34. Detailed XRD data of different phases are listed in Table 5.8. XRD analysis of the above products shows that Si-based ceramics are formed in Si-added BA charred at 1400°C. Silica in cristobalite form at 20=21.8° and carbon can be seen for all the cases. At 15% loading, the formation of SiC (JCPDS file no.29-1129) peak is more intense than for the 5% and 10% Si concentration. A peak of unreacted Si can be observed at 10% Si concentration. At 15% Si concentration, no. of Si peaks has increased, which may be due to higher concentration of Si. The peak at 20=26.6° matches with graphite (JCPDS file no.25-0284), which might have came from the graphite container or due to the graphitization of excess amorphous carbon. The peak also matched with Si\textsubscript{2}N\textsubscript{2}O (JCPDS file no. 18-1171) and SiO\textsubscript{2} (JCPDS file no. 33-1161). SiC and Si\textsubscript{3}N\textsubscript{4} can be observed at all Si concentrations. At 5% Si concentration, SiC (JCPDS file no. 29-1128) and Si\textsubscript{3}N\textsubscript{4} (JCPDS file no. 29-1132) shows two different peaks at 20=35.6° and 20=36.5°, respectively. At 10% Si concentration, SiC and Si\textsubscript{3}N\textsubscript{4} both the phases coexist at the same peak, i.e., at 20=36°. At 15% Si concentration, again SiC and Si\textsubscript{3}N\textsubscript{4} show two peaks at 20=35.6° and 20=36°, respectively. The silica and Si\textsubscript{2}N\textsubscript{2}O peak increase slightly with increase in Si concentration, which may be due to the release of oxygen during the formation of Si\textsubscript{2}N\textsubscript{2}O and its subsequent reaction with silicon to form amorphous silica according to the reactions:

\begin{align*}
2(\text{SiO}) + (\text{N}_2) &\rightarrow \langle \text{Si}_2\text{N}_2\text{O} \rangle + \frac{1}{2}(\text{O}_2) \quad \cdots \quad (4) \\
\langle \text{Si} \rangle + 2\left(\frac{1}{2}\text{O}_2\right) &\rightarrow \langle \text{SiO}_2 \rangle \quad \cdots \quad (5)
\end{align*}

When silicon powder is added to BA powder, silicon reacts with silica to produce SiO gas as per the reaction:

\begin{align*}
\langle \text{SiO}_2 \rangle + \langle \text{Si} \rangle &\rightarrow 2(\text{SiO}) \quad \cdots \quad (6)
\end{align*}

Increased SiO content in the gas upon reaction with available carbon tends to form β-SiC and α-Si\textsubscript{3}N\textsubscript{4} as per the following reactions: [34, 40]:

\begin{align*}
\text{SiO}(g) + 2\text{C}(s) &\rightarrow \text{SiC}(s) + \text{CO}(g) \quad \cdots \quad (7) \\
3\text{SiO}(g) + 3\text{C}(s) + 2\text{N}_2(g) &\rightarrow \text{Si}_3\text{N}_4(s) + 3\text{CO}(g) \quad \cdots \quad (8)
\end{align*}

The $p_{\text{SiO}}/p_{\text{N}_2}$ ratio is sufficient to favour the formation of SiC and Si\textsubscript{3}N\textsubscript{4} till 10% Si concentration. So, peaks of SiC and Si\textsubscript{3}N\textsubscript{4} increase till 10% Si concentration. As the cap of the crucible was
open, CO gas could be removed easily under the flowing N₂ atmosphere which may help for the formation of Si₃N₄. At 15% Si concentration, the intensity of SiC and Si₃N₄ is lower with respect to 5% and 10%. This may be due to the presence of higher Si concentration. Excess evolution of SiO gas may suppress the reaction; hence formation of SiC and Si₃N₄ might have reduced. From Table 5.8, it can be observed that, the degree of crystallization of silica decreases slightly with increase in Si concentration. As per reactions (4) and (5), increase in Si concentration generates more amorphous silica, which might have reduced the crystallite size. Change in crystallite size of SiC and Si₃N₄ may be due to the phase transformations. Crystallite sizes of Si₃N₂O have increased till 10% Si concentration, then remain the same at 15% Si concentration.

Fig. 5.34 XRD patterns of BA+Si (5-15%) fired at 1400°C with 1h holding time in N₂ atmosphere
Table 5.8. X-ray diffraction data for phase analysis as a function of Si concentration (%)

<table>
<thead>
<tr>
<th>% Catalyst</th>
<th>$\theta$ (deg.)</th>
<th>Interplanar spacing ‘d’ (Å)</th>
<th>Intensity (cps)</th>
<th>h k l</th>
<th>Full Width Half Maxima ‘FWHM’ (deg.)</th>
<th>Crystallite Size (Å)</th>
<th>Identified Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>21.883</td>
<td>4.06</td>
<td>2160.13</td>
<td>101</td>
<td>0.1968</td>
<td>411.2</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>26.59</td>
<td>3.36</td>
<td>1735.79</td>
<td>101,002,111</td>
<td>0.1771</td>
<td>461.12</td>
<td>SiO$_2$, Si$_2$N$_2$O</td>
</tr>
<tr>
<td></td>
<td>35.66</td>
<td>2.51</td>
<td>358.21</td>
<td>102</td>
<td>0.2362</td>
<td>353.43</td>
<td>SiC</td>
</tr>
<tr>
<td></td>
<td>36.50</td>
<td>2.46</td>
<td>178.73</td>
<td>210</td>
<td>0.1181</td>
<td>708.76</td>
<td>Si$_3$N$_4$</td>
</tr>
<tr>
<td>10%</td>
<td>21.897</td>
<td>4.059</td>
<td>4565.68</td>
<td>101</td>
<td>0.2362</td>
<td>342.61</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>26.60</td>
<td>3.35</td>
<td>2242.37</td>
<td>101,002,111</td>
<td>0.1181</td>
<td>691.49</td>
<td>SiO$_2$, Si$_2$N$_2$O</td>
</tr>
<tr>
<td></td>
<td>36.03</td>
<td>2.492</td>
<td>515.65</td>
<td>100,210</td>
<td>0.2362</td>
<td>322.71</td>
<td>SiC, Si$_3$N$_4$</td>
</tr>
<tr>
<td>15%</td>
<td>21.854</td>
<td>4.066</td>
<td>3331.29</td>
<td>101</td>
<td>0.2558</td>
<td>316.34</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td></td>
<td>26.556</td>
<td>3.356</td>
<td>1145.82</td>
<td>002,111</td>
<td>0.1181</td>
<td>691.49</td>
<td>Si$_2$N$_2$O,C</td>
</tr>
<tr>
<td></td>
<td>35.586</td>
<td>2.522</td>
<td>915.78</td>
<td>202</td>
<td>0.1771</td>
<td>471.24</td>
<td>SiC</td>
</tr>
<tr>
<td></td>
<td>35.972</td>
<td>2.496</td>
<td>588.76</td>
<td>102,210</td>
<td>0.1181</td>
<td>707.49</td>
<td>Si$_3$N$_4$</td>
</tr>
</tbody>
</table>

Fig. 5.35 shows the SEM analysis of BA+Si (5-15%) fired at 1400°C with 1h holding time in N$_2$ atmosphere. Whiskers can be observed for all the cases at 5-15% Si concentration. For 5% Si concentration, the whiskers are long and thin. At 10% Si concentration, very fine and smaller whiskers can be observed. As the Si concentration increases to 15%, both whiskers and particles can be observed. Maximum whiskers can be observed at 10% Si concentration, which may be due to the formation of SiO gas, which is sufficient for the reactions to occur freely. EDS analysis (Fig. 5.36) of this 10% Si concentration was carried out to confirm the presence of Si, O, C and N. At 15% concentration, the reactions are suppressed due to evolution of excess SiO gas. Formation of granules can be observed at 15% concentration.

Fig. 5.37 shows the FT-IR analysis of BA+Si (5-15%) fired at 1400°C with 1h holding time in N$_2$ atmosphere. The absorption bands near 1100 cm$^{-1}$ and 460 cm$^{-1}$ confirm the presence of Si-O bonding. The peak near 790 cm$^{-1}$ shows the presence of Si and C bonding. The absorption band near 650 cm$^{-1}$ shows the presence of Si-N bonding [35, 44]. The Si-O bonding was wider at 5%, but with increase in Si concentration, peaks become narrower. No remarkable changes of Si-C and Si-N bonding can be observed.
Fig. 5.35 SEM analysis of BA+Si (5-15%) fired at 1400°C with 1h holding time in N₂ atmosphere.

Fig. 5.36 EDS analysis of BA+Si (10%) fired at 1400°C for 1h in N₂ atmosphere.
Fig. 5.37 FT-IR analysis of BA+Si (5-15%) fired at 1400°C with 1h holding time in N₂ atmosphere