CHAPTER 2

SYNTHESIS AND CHARACTERISATION OF SILICON NITRIDE AND SILICON CARBIDE WHISKERS

2.1 INTRODUCTION

Silicon nitride and silicon carbide in whisker form are excellent reinforcement materials in ceramic and glass matrix composites. Lightweight metal matrix composites such as aluminium reinforced with SiC and Si₃N₄ whiskers exhibit better thermal conductivity, oxidation resistance and impact strength (Nair et al 1985). The main hurdles in extending the applications of SiC whiskers are their limited availability and prohibitive manufacturing costs. In this study, an attempt is made to synthesis silicon nitride and silicon carbide whiskers from rice husk, an agricultural waste material.

2.1.1 Rice Husk

Rice husk is the natural sheath that forms on rice grain during the growth. Rice husk is removed during refining of rice. Rice husk is the largest by-product of rice milling and its commercial utilisation could have major impact upon the economics of rice milling and consequently upon the economy of developing countries. The rice husk constitutes one of the major waste products of the agricultural industry and presents a considerable solid waste disposal problem. Burning as a means of disposal is less than desirable due to
the airborne pollution. Returning the rice husk to the land is impractical since by the nature of the harvesting process rice husks accumulate at central locations surrounding the mills where the rice kernel is separated from the husk. This separation process does not occur in the field as with most other food grains. Thus, this particular agricultural waste product is readily available in centralized locations throughout rice producing areas of the world.

The unique characteristic of rice husk is the considerable ash content, which varies from 14 to 23%, depending upon the variety of the rice, climate, yearly fluctuations and geographical location at which the rice is grown. This ash, which is left over from the burning of the rice husk, is comprised entirely of silica. Silica becomes airborne and toxic when it burns and constitutes one of the major health hazards.

The silica in rice husk is in an extremely divided form, which renders the silica readily airborne by a burning process. However, it is the same finely divided state, which also makes silica readily available as a precursor for many useful products. Many authors like Mishra et al (1985), Chakraverty et al (1988) and James and Subbharao (1986) have concluded that rice husk is an excellent source of high-grade amorphous silica. Moreover, this silica is an excellent source of very pure silicon, useful to manufacture solar cells for photovoltaic power generation and semiconductor devices (Amick 1982, Chakraverty et al 1985, Hunt et al 1984). On the other hand, the silica/carbon mixture obtained from the thermal decomposition of rice husk under inert atmosphere is a good raw material for the synthesis of silicon nitride or silicon carbide.
Rice husk is essentially a mixture of silica, carbon and volatile matter. Rice husk usually contains about 15% silica, 38% cellulose, 22% lignin and 18% pentosan, the remainder being other organic and inorganic matter. Each half of the rice husk has two distinct aspects: the inner epidermis and the outer epidermis. The organic matter is concentrated in the inner epidermis (which is in contact with the rice kernel) in the form of fibrous and cellular matter. The inorganic part is concentrated in the outer epidermis where silica, which is in amorphous form, is mainly concentrated in the regions of the horns.

The incineration of the organic components of rice husk causes a high percentage of micro pores in the ash skeleton. This highly porous ash is a favourable raw material for the production of thermal insulation shapes. The rice husk ash has high melting point, high porosity, high specific surface area and reactivity. These properties make the ash a valuable raw material for many industries.

Sharma et al (1984) have performed a mapping of the silica distribution in the husk by energy dispersive X-ray analysis (EDAX). They have shown that silica is concentrated primarily within the outer epidermis, although a small amount has been found within the inner epidermis adjacent to the rice kernel. The white ash obtained from the combustion of this raw material at moderate temperature contains 92-97% amorphous silica and some amount of metallic impurities. Further acid leach treatment removes these impurities. The organic compounds burn off in an oxidizing atmosphere. However, they can be retained in a reducing atmosphere or non-oxidizing atmosphere even up to 800°C. This pyrolysed rice husk approximately consists of 50% silica and 50% carbon.
Real et al (1996) have obtained pure silica (99.5%) with a specific surface area approximately 260 m²/g by preliminary leaching of rice husk with a solution of hydrochloric acid before their combustion at 600°C. However, if the leaching by HCl is done after combustion of the rice husks at 600°C, amorphous silica with the same purity is obtained. However, its surface area decreases to 1.0 m²/g. This behaviour is due to a strong interaction between the silica and the potassium contained in the rice husk, which leads to a dramatic decrease in the specific surface area. This result leads to a better understanding of the effect of potassium on the morphology of silica.

Hanna et al (1985) have reported the synthesis of silicon nitride by firing treated (treatment consists of impregnating rice husk with ferrous sulphate solution) rice husk at 1200°C-1500°C for 0.5-2.0 hours in an ammonia atmosphere. The addition of iron is essential to the formation of silicon nitride from rice husk at temperature below 1500°C. There is an optimum ratio of iron to silica equivalent to 0.07 for the formation of silicon nitride. The silicon nitride produced from rice husk is mainly in the α form with small amount of β form.

Rahman and Riley (1989) have produced α-Si₃N₄ powder of high purity by nitriding pyrolysed rice husk at temperatures between 1260 and 1450°C under 95% nitrogen and 5% hydrogen. Hydrogen addition is beneficial in accelerating the rate of nitride formation. The addition of iron (III) oxide and nickel (III) oxide to the rice husk promotes the formation of silicon nitride at temperature as low as 1300°C. The other transition metal oxides have no catalytic effect on the nitridation, although vanadium (v) oxide favours the formation of β-Si₃N₄. The particle dimension of the milled rice husk determines the morphology of silicon nitride. Silicon nitride crystals of hexagonal
symmetry are obtained when the particle size of rice husk is equiaxed. However, higher particle size and lower packing density yield silicon nitride of needle morphology. Addition of silicon nitride powder seeds results in the formation of fine equiaxed silicon nitride particles.

Patel and Prasanna (1991) have reported the synthesis of silicon nitride from acid treated rice husk with an added Fe-catalyst in NH$_3$ atmosphere at 1350°C. Addition of HCl eliminates K, Na, and Fe etc as chlorides. They have also obtained Si$_3$N$_4$ without addition of catalyst. Si$_3$N$_2$O also appears along with Si$_3$N$_4$ at 1350°C and 1400°C. The formation of Si$_3$N$_4$ from rice husk has been explained by carbothermal reduction. The overall reaction is

$$3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6\text{CO} \quad (2.1)$$

In the NH$_3$ atmosphere, the different reaction steps could be conceived as follows where the gas molecules like H$_2$, O$_2$, N$_2$ and CO can participate

$$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \quad (2.2)$$

$$\text{SiO}_2 + \text{H}_2 \rightarrow \text{SiO} + \text{H}_2\text{O} \quad (2.3)$$

$$\text{SiO} + \text{H}_2 \rightarrow \text{Si} + \text{H}_2\text{O} \quad (2.4)$$

$$3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 \quad (2.5)$$

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{N}_2 \quad (2.6)$$

$$\text{Si}_3\text{N}_4 + \text{O}_2 \rightarrow \text{Si}_2\text{N}_2\text{O} + \text{SiN}_2\text{O} \quad (2.7)$$
Rahman (1994) have prepared silicon nitride by digesting rice husk using various concentrations of nitric acid at 60°C. It has been found that rice husk containing about 29% carbon and about 70% silica can be produced by digesting the rice husk in 12M HNO₃ for 3 hours. The carbon and silica obtained are in stoichiometric ratio for the overall carbothermal reduction reaction. An equiaxed, sub micrometer and high α-phase silicon nitride powder has been obtained by heating pyrolysed digested husk at about 1430°C under flowing nitrogen. The homogeneity of the carbon and silica is the main factor that allows completion of the reaction.

Raju and Verma (1997) have reported the synthesis of high purity β-SiC whisker 50-60 μm long and <1.0 μm diameter by the pyrolysis of rice husk in a reduced pressure of nitrogen at 1000 -1500°C with out the use of any external reducing agents or catalysts. Under the pyrolysis conditions, silica present in the raw material undergoes reduction to SiO (g) and Si (g) by several possible reactions, as follows, leading to the formation of SiC

\[
\text{SiO}_2 + C \rightarrow \text{SiO (g)} + \text{CO} \quad (2.12)
\]

\[
\text{SiO} + C \rightarrow \text{Si} + \text{CO} \quad (2.13)
\]
SiO + 2C → SiC + CO  \hspace{1cm} (2.14)

Si + C → SiC  \hspace{1cm} (2.15)

Silicon monoxide readily combines with the finely subdivided C resulting in the formation SiC and CO. Whisker formation is favoured more by vapour phase than by solid state reaction under the prevailing conditions of the flow of N\textsubscript{2} gas through the porous cellular structure of the rice husk. Under vacuum, the probability of formation of silicon metal is greater. Whisker formation may also have occurred by the VLS mechanism (V-vapor feed gas, L-liquid catalyst, and S- solid crystalline whisker growth) through the presence of available iron. The role played by a small amount of iron in rice husk as a catalyst is very important. The carbon and silicon atoms in the vapour state saturate in the liquid iron melt and subsequently precipitate in the form of whiskers, the iron impurity being lifted into the form of a micro ball at the whisker tip.

Markovska et al (1998) have studied the phase transformations in the rice husk system during high temperature treatment in nitrogen. The type of amorphous SiO\textsubscript{2} introduced, the quantity and ratio between initial components and the type of atmosphere in which the interactions are taking place mainly influence the formation of oxygen free phases.

Si\textsubscript{3}N\textsubscript{4} whiskers are formed when synthesized from pyrolysed rice husk. SiC whiskers are also formed from pyrolysed rice husk at elevated temperatures (Patel and Karera 1987). The pyrolysed rice husk contains fibres, which can serve as substrates for initiation and growth of whiskers. The fibres present in the initial as well as in the coked rice husk can exist even at high
temperatures (≥1300°C) and participate as a substrate in the formation of SiC whiskers (Krishnarao et al 1991). On the other hand, Patel and Prasanna (1990) have reported that SiC produced from acid treated rice husk presents no fibre structure. Digestion of the husk in strong acid media causes a severe reaction with fibres and degrades them to agglomerates or to particles. Consequently, the substrate mechanism observed in coked rice husk cannot take place in acid treated rice husk.

Padmaja and Mukunda (1999) have investigated the sequence of transformations and the mechanism of crystalline silica, carbon and silicon carbide from rice husk. The structural evolution of silicon carbide particulates during the conversion process has been critically examined.

The reaction between silica and carbon leads to a weight loss owing to the formation of CO/CO₂ gases depending on the extent of reaction. According to stoichiometry, there should be a weight loss of 56% for the reaction to reach completion:

\[
\text{SiO}_2 (s) (60\text{gms}) + 3\text{C}(s) (36\text{gms}) \\
\rightarrow \text{SiC}(s) (40\text{gms}) + 2\text{CO} (g)(56\text{gms}) \\
\]

The composition of black ash is approximately 55% SiO₂ and 45% C. In the present case, the pyrolysed product contains at least 25%/(12/(12+37)) excess carbon/graphite in it for the reaction to reach completion.

\[
\text{SiO}_2 (s) (55\text{gms}) + 3\text{C}(s) (45\text{gms}) \\
\rightarrow \text{SiC}(s) (37\text{gms}) + 2\text{CO} (g)(51\text{gms}) \\
+ 12\text{g (excess carbon)}
\]
Except for the gradual change in the morphology leading to the formation of dense crystals of $\beta$-SiC, formation of $\alpha$-SiC has not been seen. The fine particle size of $\beta$-SiC, formed at lower reaction temperatures, apparently precluded the transformation of $\alpha$-SiC.

2.1.2 Carbothermal Reduction

Silicon nitride is manufactured by the carbothermal reduction and nitridation of silica according to the overall reaction

$$3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6\text{CO} \quad (2.18)$$

The theoretical yield of $\text{Si}_3\text{N}_4$ calculated from the above reaction is 44.4% (assuming that C and $\text{SiO}_2$ are in stoichiometric ratio). Reaction (2.18) is moderately endothermic, requiring energy approximately 1268 kJ/mol of silicon nitride at 1427°C. Komeya and Inoue (1975) have prepared $\alpha$-$\text{Si}_3\text{N}_4$ powder from silica at $\text{C}/\text{SiO}_2 = 2$-20, at 1400 - 1450°C. They conclude that the reaction rate significantly increase with increase in carbon content and surface area of the raw powders. Mori et al (1983) have reported that a complete conversion of very fine silica to $\alpha$-$\text{Si}_3\text{N}_4$ is achieved at $\text{C}/\text{SiO}_2 = 5$ and 15 after 10h at 1500°C. Zhang and Cannon (1985) have reported that the reaction rate increase with increase in surface area of silica and carbon. They have concluded that homogeneous mixing and the addition of excess carbon contribute to the completeness of the carbothermal reduction and nitridation of silica at 1400°C.

Ekelund and Forslund (1992) have confirmed that the addition of excess carbon and a high surface area of the reactant are important in attaining uniform contact between silica and carbon particles. Nucleation can be increased by
either increasing the starting C/SiO₂ ratio (Cho and Charles 1991), increasing the specific surface area of carbon source, increasing the intimacy between C and SiO₂ (Vlasova et al 1995) or a combination of these. Sanyal et al (1991) have reported that in the presence of iron the amount of β Si₃N₄ above 1300°C increases with temperature. The preponderance of β Si₃N₄ over the α form at a higher reaction temperature was assumed to be related to the formation of a Fe-Si-N liquid. In the presence of impurities such as Fe, Fe₂O₃, CaO and V₂O₅, β-Si₃N₄ formation (Bandyapadhyay and Mukherji 1991) is associated with the existence of low melting eutectics.

The reaction involves multiple steps and to begin with the reduction of silica by carbon in direct physical contact according to

\[ C + SiO₂ \rightarrow SiO + CO \] (2.19)

\[ C + SiO₂ \rightarrow SiO + CO₂ \] (2.20)

\[ C + CO₂ \rightarrow 2CO \] (2.21)

The α-Si₃N₄ can be formed by heterogeneous nucleation according to reaction (2.22). The growth occurs by gas phase process according to reaction (2.23):

\[ 3C + 3SiO + N₂ \rightarrow Si₃N₄ + 3CO \] (2.22)

\[ 3SiO + 3CO + N₂ \rightarrow Si₃N₄ + 3CO₂ \] (2.23)
The exact reaction mechanism is undefined and there is disagreement in the formation of α-Si$_3$N$_4$ by a gas phase reaction involving SiO. In general, the morphology of the α-Si$_3$N$_4$ crystallites bears no resemblance to either the starting C or SiO$_2$ crystallites (Weimer et al 1999).

The addition of small amount of Si$_3$N$_4$ seed to the starting C/SiO$_2$ precursor has a substantial effect on both the reaction rate and product morphology. In addition, seeding makes the reaction insensitive to the precursor ratio C/SiO$_2$ because the presence of seed precludes the need for nucleation to occur. The significant increase in reaction rate is observed with the addition of seed (Figusch and Licko 1987). There is some indication that the intensity of the seeding effect increases with increasing surface area of seeding powder (Licko et al 1992).

Kinetically, the overall reaction (2.18) is slow, requiring many hours to complete. This is due to a thermodynamic upper temperature limit of 1450°C at nitrogen pressure of 0.1 MPa for the formation of Si$_3$N$_4$. It is demonstrated (Ekelund and Forslund 1990) that α-Si$_3$N$_4$ can be synthesised at a temperature as high as T = 1680°C when operating under a N$_2$ pressure of approximately 6 MPa.

Thermodynamically, CO is detrimental to the process, as the overall reaction is reversible. An increase in CO will hinder the desired forward nitriding reaction. The SiO$_2$ becomes stable when the CO partial pressure rises about $p_{co}$=34.9 kPa, even when the temperature is less than 1450°C.

Excess N$_2$ flow above the stoichiometric requirement reduces the CO concentration and has been shown to be effective in reducing the time required
to achieve complete conversion of SiO₂. Although higher N₂ flows are desirable to reduce CO concentrations, too high a flow may reduce the yield of Si₃N₄ by promoting the loss of volatile SiO from the reaction system (Mori et al 1983). Such SiO may present operating complications such as the deposition of volatile SiO on cooler surfaces near the exit of furnace. (Ekelund and Forslund 1990).

Reduction of SiO₂ with low purity pigment black is much faster than with high purity acetylene black because of the presence of transition metal impurities in the carbon (Licko et al 1992).

The carbothermal nitridation using ammonia (NH₃) instead of N₂ has been found to enhance dramatically the nitride formation (Durham et al 1988). It is believed that dissociation of NH₃ to active molecular nitrogen and hydrogen with smaller amounts of NH, NH₂ and N₂ increase the reaction rate. The addition of H₂ to reactant N₂ has also been found to accelerate nitride formation (Rahman and Riley 1989) although its addition at reaction temperatures may promote the formation of SiC (Li et al 1983).

SiC synthesis is favoured at higher temperatures (T>1500°C) where the reaction rate is faster. The overall reaction is as follows:

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

(2.24)

Under the pyrolysis conditions, silica present in the raw material undergoes reduction to SiO (g) and Si (g) by several possible reactions leading to the formation of SiC.
\[
\text{SiO}_2 + \text{C} \rightarrow \text{SiO (g)} + \text{CO} \quad (2.25)
\]
\[
\text{SiO} + \text{C} \rightarrow \text{Si} + \text{CO} \quad (2.26)
\]
\[
\text{SiO} + 2\text{C} \rightarrow \text{SiC} + \text{CO} \quad (2.27)
\]
\[
\text{Si} + \text{C} \rightarrow \text{SiC} \quad (2.28)
\]

Most of the research work for increasing the rate of reaction has focused on operating at higher pressures, removing by-product CO, adding nuclei to the precursor and reacting with more active species such as those produced by decomposition of NH\textsubscript{3} (Rahman & Riley 1989). Silicon carbide whiskers can also be synthesised from silicon nitride powders.

The basic process for producing SiC whiskers can be simplified into three primary stages: pre-conversion stage, conversion stage and post-conversion quality enhancement stage. There are numerous ways to prepare raw materials for the conversion stage, including calcining, coking, extruding, drying, mixing, kneading, pulverising, acid leaching, and addition of a catalyst. The steps to be used are determined by the raw materials used. Various sources of silica are available, including amorphous silica, sand, glass powder, silica gel, and rice hulls/husk.

The conversion stage has fewer variations possible. Typically, it is completed in a high-temperature furnace with an inert atmosphere. The temperature cycle can involve temperatures anywhere from 800 to 1600°C, although some exposure to the higher temperatures in this range is essential for completion of the reaction. Post conversion processes are necessary to separate
whiskers from the particulates and to enhance the quality of whiskers produced. Such processes include froth floatation, carbon removal and particle recovery.

Silicon carbide whiskers can also be synthesised from mixtures of silicon nitride and graphite (Wang et al 1992). Silicon nitride is carbothermally reduced with graphite in the system at temperatures ranging from 1400 to 1700°C. The content of silicon carbide increases with increasing temperature. The formation of silicon carbide is related to the surface silica contained in the silicon nitride powder and it involves the volatilisation of the surface silica to form silicon monoxide that reacts with graphite to produce carbon monoxide (Calquhoun et al 1973). The latter in turn carburises the silicon nitride to silicon carbide.

\[
3\text{CO} + \text{Si}_3\text{N}_4 \rightarrow 2\text{SiC} + 2\text{N}_2 + \text{CO}_2 + \text{SiO} \tag{2.29}
\]

From experimental results however, it has been proposed by Wang and Fischman (1991) that the formation of silicon carbide is related to the decomposition of silicon nitride. The decomposition reaction is

\[
\text{Si}_3\text{N}_4(s) \rightarrow 3\text{Si}(s) + 2\text{N}_2(g) \tag{2.30}
\]

The significant weight loss in argon atmosphere, as a result of following reaction started at about 1300°C.

\[
\text{Si}_3\text{N}_4 \rightarrow 3\text{Si}(s) + 2\text{N}_2 (g) \tag{2.31}
\]

Above the melting point of Si (1410°C) Si (l) can react with graphite to form silicon carbide.
Si (l) + C \rightarrow SiC(s)  \hspace{1cm} (2.32)

This is in agreement with the observation that silicon carbide started to form at temperature from 1400 to 1450°C. Reaction (2.31) will drive the conversion from silicon nitride to silicon carbide if carbon is available in sufficient quantity. However, insufficient carbon leads to residual silicon.

2.1.3 Design of Experiment

In this chapter, an attempt has been made to synthesis silicon nitride and silicon carbide whiskers from rice husk. Silicon carbide whiskers were also synthesised from silicon nitride powders.

Rice husk was characterised for silica and other metallic impurities. IR, XRD, TGA, DSC, DTA, surface area and microstructure of rice husk were carried out. Silicon nitride whiskers were synthesised from raw rice husk by firing at 1400°C in a flowing N\textsubscript{2} atmosphere with and without additive. The phase formation of silicon nitride was confirmed by XRD. Surface chemistry was studied by XPS. SEM studies were carried out to study the morphology. The role of metallic impurity on the morphology and conversion were studied.

Silicon carbide whiskers were synthesised from raw rice husk. The firing was done at 1600°C in a coke bed atmosphere without any additives. XRD was taken to confirm the phases. SEM was used to study the morphology. Silicon carbide whiskers were also synthesised from silicon nitride and graphite at 1600°C in a coke bed atmosphere. XRD confirmed the presence of β-SiC. SEM revealed the whisker morphology of SiC.
2.2 EXPERIMENTAL PROCEDURE

2.2.1 Characterisation of Rice Husk

The rice husk was washed well with distilled water to remove water-soluble impurities. It was dried in an oven at 110°C for 24 hours to remove moisture. The thoroughly dried rice husk was ground in an attrition mill using alumina-grinding balls. The impurities present were investigated by Atomic Absorption Spectroscopy (AAS) and Induction Coupled Plasma (ICP) techniques. The surface area was measured by Brunnauer-Emmett-Teller (BET) method.

Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on DSC-TGA (Model STA 409C, Stanton-Redcroft Ltd., London, U.K.) Small amounts of powder weighing 10-12 mg were heated at the rate of 10°C/min from room temperature to 1400°C in static air conditions. Differential thermal analysis (Model 1700, Perkin Elmer, U.K.) was carried out on rice husk. Small amounts of powder weighing 10-12 mg were heated at the rate of 20°C/min from room temperature to 1350°C in nitrogen atmosphere.

The potassium bromide disk technique was used in the present IR study. Infra red spectra were recorded by means of spectrophotometer (Model 397, Perkin Elmer, U.K.). The various spectral bands were identified from the literature. The base line technique was adopted for the determination of absorbencies. The microstructure of rice husk was studied by scanning electron microscope (SEM).
2.2.2 Synthesis of Silicon Nitride Whiskers

The silicon nitride whiskers were synthesised by carbothermal reduction and nitridation as explained in the figure 2.1. The ground rice husk was taken in graphite containers and fired at 1400°C for six hours. The nitrogen flow started from 50°C with 2l/minute flow rate. The heating rate was 7°C/minute. The samples were cooled naturally. After firing it was decarbonised at 600°C to remove any residual carbon present. The synthesis is carried out with and without additive. The sample without any external additive is denoted as sample A and sample with 2% antimony additive is denoted as sample B.

2.2.3 Characterisation of Silicon Nitride Whiskers

X-Ray Diffraction (XRD, Philips, Holland) analyses of nitrided samples were carried out using Ni filtered Cu-Kα radiation (40kV, 20mA). The examination was made between 2θ=5-90° with a scanning speed of 2°min⁻¹.

Infra red spectra over the range 400-4000cm⁻¹ were recorded by means of spectrophotometer (Model 397, Perkin Elmer, U.K.). The potassium bromide disk technique was used in the present IR study. The various spectral bands were identified from the literature. The base line technique was adopted for the determination of absorbencies.

The density was measured by specific gravity bottle method. The surface area was measured by Branauer-Emmet-Teller (BET) method, using N₂ as an adsorbate, using micromeritics chemisorb 1200. X-ray Photo-electron spectroscopy (XPS) is an important analytical technique for surface and thin
Figure 2.1  Flow chart for the synthesis of silicon nitride whiskers from rice husk
film characterisation of solid materials. It provides qualitative and quantitative information relating to the outermost atom or molecule layers. The depth of information or the thickness of the analysing surface layer ranges from 1 to 3 nm. This mainly depends on the kinetic energy of the photoelectrons (Okada et al 1995). Whisker surface chemistry analysis was carried out by Mgkα X-ray photoelectron spectroscopy (XPS). The energy scale was calibrated by assigning the energy of the most intense carbon peak to that of the carbon (282.4 eV). The spectrum recorded was an overall binding energy scan from 1000 to 0 eV and was used to identify the elements present.

Scanning Electron Microscopy (SEM) (JEOL JSM 5300) was used to study the microstructure of the samples. The powder coated with a thin layer of gold using a sputter coater was mounted with the stub in the specimen chamber of the scanning electron microscope (SEM). The secondary electron signals carry the information about the surface structure, size, and shape of the whiskers.

2.2.4 Synthesis of Silicon Carbide Whiskers

An alumina tube of 225mm height, 70 mm hole of inner diameter and 35 mm wall thickness was used as a container. One side of the tube was sealed with an alumina plate and a coke bed was created. Above this bed, pyrolysed rice husk was placed. The top was sealed with alumina plate using appropriate mortar. There was no room for leakage and a coke atmosphere was created inside the nozzle. The nozzle was fired at 1600°C/3hours. (Sample Identification No. C) Some attempts were made to grow in-situ silicon carbide whiskers using silicon nitride and graphite powder in the molar ratio 3:1 and
fired at 1600°C/3 hours. (Sample Identification No.D). The flow chart for the synthesis of silicon carbide is shown in figure.2.2

2.2.5 Characterisation of Silicon Carbide Whiskers

The X-ray powder diffraction analysis was carried out using CuKα radiation with a Ni target (Philips Diffractometer, Holland). The density of the material was determined by specific gravity bottle method. The surface area was measured by BET method, using N₂ as an adsorbate using micromeritics chemisorb 1200.

Infra red spectra over the range 400-4000cm⁻¹ were recorded by means of spectrophotometer (Model 397, Perkin Elmer, U.K.). The potassium bromide disk technique was used in the present IR study. Scanning electron Microscopy (SEM) (JEOL JSM 5300) was used to study the microstructure of the samples.

2.3 RESULTS AND DISCUSSION

2.3.1 Rice Husk

The silica content in rice husk by gravimetric method is 18%. The surface area of rice husk by BET method is 0.93 m²/g. Table.2.1 illustrates the trace elements present in the raw rice husk.
Figure 2.2 Flow chart for the synthesis of silicon carbide whiskers

- RICE HUSK
- WASHING
- MILLING <300 μm
- Carbothermal Reduction in Coke Bed Atmosphere (1600°C/3 hours)
- Decarbonisation (650°C in air)
- Characterisation

- Silicon Nitride & Graphite 3:1 Molar Ratio
- Mixing

Methods:
- XRD
- IR
- XPS
- SEM
- Physical Properties
Table 2.1 Trace elements in rice husk

<table>
<thead>
<tr>
<th>Trace elements</th>
<th>Amount (ppm)</th>
</tr>
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<tbody>
<tr>
<td>Al (ICP)</td>
<td>367</td>
</tr>
<tr>
<td>Fe (ICP)</td>
<td>14</td>
</tr>
<tr>
<td>Ca (ICP)</td>
<td>43</td>
</tr>
<tr>
<td>Mg (AAS)</td>
<td>890</td>
</tr>
<tr>
<td>Zn (AAS)</td>
<td>231</td>
</tr>
<tr>
<td>Cu (AAS)</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Thermo gravimetric Analysis (TGA) in Figure 2.3 indicates the weight loss against temperature of raw rice husk in air. Differential scanning calorimetry analysis is shown in Figure 2.4. The TGA curve shows that weight loss in the first stage takes place in the range 40 to 150°C. The DTG curve exhibits a peak at 87.6°C. The DSC curve also exhibit an endothermic peak at 94.8°C. The mass loss around 6.58% in this stage may be attributed to the removal of moisture from rice husk.

The second stage is identified as a plateau in the TG curve in the range 150-220°C with a mass loss of 4.28% while DTG and DSC curves do not show any peak at this stage. This may be considered as a transition stage.

The third stage of decomposition takes place in the range 220 to 400°C indicating a steep fall and a sharp peak in the TG and DTG curves respectively. The mass loss associated with this stage is 46.28% and this may be due to removal of volatile matter (Real et al 1996). The corresponding exothermic peak in DSC is observed at 294.2°C.
Figure 2.3  TGA curve of raw rice husk.
Figure 2.4 DSC curve of raw rice husk.
The fourth stage of mass loss (31.51%) in the range 350-900°C corresponds to combustion process. The DTG shows a gradual decrease in the rate of mass loss and DSC shows an exothermic reaction.

Among the four stages, the major decomposition has occurred in the third and fourth stages. The temperature range of fourth stage is higher and the rate of mass loss is slower as compared to the third stage.

The TGA and DSC analyses reveal distinct stages of mass loss mainly due to the removal of moisture, release of volatile matter and burning of combustible material. DSC records an exothermic reaction during the course of thermal decomposition and endothermic peak during the removal of moisture.

Differential Thermal Analysis (DTA) is performed under a nitrogen atmosphere from ambient temperature to 1350°C. The DTA curve of raw rice husk (Figure 2.5) indicates a peak between 800 - 900°C and a peak around 1200°C. The initial exothermic peak shows the pyrolysis of rice husk and second peak confirms the onset of nitridation. When rice husk is fired under inert atmosphere, the peak for thermal decomposition and combustion shifts towards higher side of temperatures (Padmaja and Mukunda 1999)

The IR spectrum of rice husk (Figure 2.6) reveals the presence of silica by the peak at wavelength 456 cm\(^{-1}\). The peak at 790 cm\(^{-1}\) is considered to be due to Si-O/Si-C bonding. The peak in the range 1326-870 cm\(^{-1}\) indicates the presence of Si-O-Si, CO, C-C bonds. The peaks seen at 1600 cm\(^{-1}\) and 3400 cm\(^{-1}\) are due to the presence of entrapped water molecules (Cooper 1992).
Figure 2.5 DTA curve of raw rice husk.
IR spectrum of raw rice husk.
Figure 2.7 presents the SEM micrograph of fibrous skeleton of rice husk, which acts as a substrate for the growth of silicon nitride whiskers. The cellulose skeleton is clearly visible in the micrograph.

2.3.2 Silicon Nitride Whiskers

Table 2.2 gives the general properties of A and B samples.

<table>
<thead>
<tr>
<th>Properties</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Morphology</td>
<td>Rod</td>
<td>Rod</td>
</tr>
<tr>
<td>Specific gravity (g/cc)</td>
<td>2.75</td>
<td>2.86</td>
</tr>
<tr>
<td>Diameter (μm)</td>
<td>0.5-2</td>
<td>0.5-2</td>
</tr>
<tr>
<td>Length (μm)</td>
<td>5-250</td>
<td>5-250</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>20-250</td>
<td>20-250</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>2.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

2.3.2.1 Phase and Structural Analysis

The results from XRD studies for samples A and B are given in Figures 2.8 (A & B) respectively. Silicon oxynitride is the major phase obtained from rice husk without additives (sample A), whereas silicon nitride is the major phase obtained from rice husk with addition of antimony (sample B). In Figure 2.8, sample A exhibits Si₂N₂O peaks in the (111), (020), (002) and (110) directions at d (Å) = 3.36, 4.42, 2.42 &4.62 respectively. Trace of β Si₃N₄ is also present. In sample B where rice husk is added with 2% antimony, all the
Figure 2.7 SEM micrograph of raw rice husk.
Figure 2.8 XRD pattern of silicon nitride (Samples A & B).
major peaks belong to $\alpha$-Si$_3$N$_4$. It is to be noted only one peak of Si$_2$N$_2$O corresponding to $d=4.41$ Å is present with low intensity.

The IR spectrum of sample A (figure 2.9) does not show any peak at 790 cm$^{-1}$. Three sharp peaks in 800-350 cm$^{-1}$ are related to the bending vibrations of Si-N-Si and N-Si-N bonds. The peak at 1089 cm$^{-1}$ in rice husk has disappeared and Si $^{4+}$ (of SiO) and N$_2$ reacted to form silicon nitride. The appearance of peaks at 600, 688 and 1040 cm$^{-1}$ corresponds to $\alpha$-Si$_3$N$_4$. The sharp peaks are characteristics of the covalent bonds of silicon nitride (Patel and Prasanna 1991).

### 2.3.2.2 Surface Chemistry

Samples A & B are thus scanned for the major peaks of interest, the Si 2p peak (102.25 eV), the C 1s peak (284.6 eV), the N 1s peak (397.0 eV) and O peak (531.0 eV). Table 2.3 & 2.4 gives the XPS results of sample A & B.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Expected Position (eV)</th>
<th>Measured Position (eV)</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>284.6</td>
<td>284.6</td>
<td>Carbon/hydrocarbons</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.8</td>
<td>103.9</td>
<td>Silicon oxynitride</td>
</tr>
<tr>
<td>Si 2p</td>
<td>104.0</td>
<td>104.6</td>
<td>Silica</td>
</tr>
<tr>
<td>N 1s</td>
<td>398.4</td>
<td>397.0</td>
<td>Silicon oxynitride</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.4</td>
<td>532.1</td>
<td>Oxygen</td>
</tr>
</tbody>
</table>
Figure 2.9  IR spectrum of silicon nitride (Sample A).
Table 2.4 XPS results of sample B

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Expected Position (eV)</th>
<th>Measured Position (eV)</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>284.6</td>
<td>284.6</td>
<td>Carbon/hydrocarbons</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.8</td>
<td>102.25</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>N 1s</td>
<td>398.4</td>
<td>397.0</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.4</td>
<td>532.1</td>
<td>Oxygen</td>
</tr>
</tbody>
</table>

The surface chemistry of the whisker is a very important parameter in defining the utility of the whisker to toughen materials (Schmidt et al 1995). The evaluation of silicon peak at 104.6 eV shows the amount of oxidised Si ($SiO_2$ at 104.6eV) in reference to the nitrogen bonded Si ($Si_3N_4$ at 102.8eV). This proves that silicon nitride whiskers synthesised without catalyst has a higher amount of an oxidised phase on the particles surface compared to the silicon nitride whiskers with antimony as catalyst.

2.3.2.3 Microstructure

Figure 2.10(a) shows SEM micrograph of the sample fired at 1400°C/1 hour in nitrogen atmosphere. It indicates the beginning of the formation of elongated structures. Figure 2.10(b) shows the SEM micrograph of sample fired at 1400°C/6 hours in nitrogen atmosphere. It is interesting to note the rod morphology and the elongation in a-b direction. Further reaction would probably make the surface smoother.

Figure 2.11(a) shows the bamboo joint morphology. The morphology of whiskers ranges from straight smooth surfaced to curved whiskers. Figures 2.11 (a) and (b) shows the curved whisker morphology of sample B at
Figure 2.10 SEM micrographs of silicon nitride (Sample A)
(a) Nucleation of elongated rods
(b) Rod morphology
Figure 2.11  SEM micrographs of silicon nitride (sample B)

(a) Bamboo joint morphology
(b) Curved whisker morphology
lower and higher magnifications respectively. It has been observed that the whiskers are well developed.

2.3.3 Silicon Carbide Whiskers

Rice husk fired at 1600°C fully converts to whiskers without any particulate matter. The general properties of silicon carbide whiskers synthesised from rice husk fired at 1600°C (sample C) and synthesised from silicon nitride and graphite powders (sample D) are given in Table 2.5.

<table>
<thead>
<tr>
<th>Properties</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morphology</td>
<td>Rod</td>
<td>Rod</td>
</tr>
<tr>
<td>Specific gravity (g/cc)</td>
<td>2.75</td>
<td>3.0</td>
</tr>
<tr>
<td>Diameters (µm)</td>
<td>0.1-1.0</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Length (µm)</td>
<td>50-100</td>
<td>50-200</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>5-100</td>
<td>5-200</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>2.7</td>
<td>2.65</td>
</tr>
</tbody>
</table>

2.3.3.1 Phase and Structural Analysis

In the X-ray diffractogram of sample C (Figure 2.12), intense peaks in the (111), (220) and (200) directions from β-SiC are observed with out significant presence of other crystalline phases such as free silica, carbon and mullite. In the reaction conditions, β-SiC is obtained in the form of whiskers of cubic crystal structure with (111) directional growth. Information available in the literature reveals that pyrolysis of rice husks give rise to material
Figure 2.12 XRD pattern of silicon carbide from rice husk (Sample C).
predominantly rich in $\beta$-SiC in both whisker and particulate forms. This is potentially important as it is reported that $\beta$-SiC is less brittle and less susceptible to damage during fabrication in comparison with the $\alpha$ form.

The IR spectrum of sample C is shown in Figure 2.13. The IR band resulting from deformation vibrations at 470 cm$^{-1}$ belongs to Si-O-Si, Si-O-C, C-C stretching vibrations. Band at 794 cm$^{-1}$ can be ascribed to vibrational modes of Si-C. The absence of any band in the range 1214-1220 cm$^{-1}$ indicates the absence of amorphous silica (Raju and Verma 1997).

In the X-ray diffractogram of sample D (figure 2.14), intense peaks in the (111), (220) and (200) directions from $\beta$-SiC are observed with minor phase of $\alpha$Si$_3$N$_4$.

2.3.3.2 Microstructure

There is a distinct difference in the morphology of whiskers grown from rice husk and whiskers grown from silicon nitride. Although both exhibit rod like structure, whiskers grown from rice husk are curved whereas whiskers grown from silicon nitride are straight and smooth.

Figure 2.15 shows the morphology of silicon carbide whiskers grown from rice husk (sample C). Figure 2.15(a) shows the general morphology of SiC whiskers. Figure 2.15(b) shows that the whiskers are not very straight and smooth. Figure 2.15(c) shows the ribbon morphology of very fine whiskers. Figure 2.15(d) shows the impurities present on the surface of the whiskers. However, this type of morphology is seen only once in the whole of the sample.
Figure 2.13 IR spectrum of silicon carbide (Sample C).
Figure 2.14 XRD pattern of silicon carbide from silicon nitride (Sample D).
Figure 2.15  SEM micrographs of silicon carbide from rice husk (Sample C)
(a) General morphology
(b) Morphology of slightly bent whiskers
(c) Ribbon morphology of whiskers
(d) Impurities on the surface of a whisker
The growth of whiskers probably also occurs by the VLS mechanism through the agency of iron impurity in the rice husk acting as the liquid catalyst.

Figure 2.16 shows the morphology of silicon carbide whiskers grown from silicon nitride. Figure 2.16(a) shows the bamboo joint morphology. Figure 2.16(b) shows very straight and parallel whiskers. The surface of the whiskers is also very smooth. Figure 2.16(c) shows the branching of the whiskers. In general, all the whiskers are dense. There is no hollow whisker present. This is confirmed by Figure 2.16 (d). No droplets are found in SiC synthesised from silicon nitride, indicating that those whiskers are formed by a mechanism different from the conventional vapour-liquid-solid mechanism.

2.4 CONCLUSIONS

1. It is seen that oxygen containing phases like Si$_3$N$_2$O usually forms from a precursor material like rice husk where SiO$_2$ is present in amorphous form. Any metallic impurity like antimony added as catalyst always helps in the formation of either silicon nitride or carbide depending upon the firing temperature and atmosphere. It is interesting to note that although oxygen-containing phases like Si$_3$N$_2$O are formed, SiO$_2$ is not seen in the XRD results.

2. The reactivity of silica is enhanced in the presence of a metallic catalyst and lead to the formation of oxygen free phases. Therefore the catalyst addition, fibrous nature of the raw material, temperature and atmosphere plays important role in determining the morphology and surface chemistry of oxygen free phases.
Figure 2.16 SEM micrographs of silicon carbide from silicon nitride (Sample D)
(a) General morphology
(b) Morphology of straight and smooth whiskers
(c) Branching of whiskers
(d) Cross section of a whisker
3. Pyrolysis of rice husks under coke bed atmosphere leads to their conversion to SiC whiskers without the need of external source of carbon or catalyst material. The porous cellular structure of rice husk acts favourably for whisker growth.

4. The SiC formation is considered to involve formation of SiO (g) and Si (g) by carbothermal reduction of SiO₂ and subsequent reaction with finely divided carbon to form SiC. The growth of whiskers probably also occurs by the VLS mechanism through the agency of Fe impurity in the rice husk acting as the liquid catalyst.

5. No droplet is found in SiC synthesised from silicon nitride, indicating that those whiskers were formed by a mechanism different from the conventional vapour-liquid-solid mechanism.