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Development of Si_2N_2O, Si_3N_4 and SiC Ceramic Materials Using Rice Husk

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Abstract: The presence of silicon in rice husk has been established by its chemical and thermal degradation. The bonding between Si and C have been studied by IR spectroscopy. The existence of IR peak at ~800 cm^{-1} shows Si–C bonding in raw rice husk, which is shifted to 790 cm^{-1} during coking and pyrolysis. ESCA study of surface showed Si, C, O and F to be present; Si in the form of SiC_x and SiO_x and C as SiC_x and CH_x. On sputtering, the SiO_x and CH_x species decrease with increase of SiC_x level. The formation of SiC from coked rice husk and Si_3N_4 and Si_2N_2O from HCl treated rice husk has been observed at 1200–1400°C under N_2 and NH_3 atmosphere, respectively. The chemical analysis of raw rice husk and products are tabulated. The XRD analyses shows the presence of different phases in the products. A new mechanism for the development of these ceramic materials has been proposed.

1 INTRODUCTION

A large number of ceramic whiskers have been produced from various metals as well as oxides.[1–3] Rice husk is an agrowaste material composed of SiO_2, trace metals and a large number of organic molecules; being a potential source for the production of Si_2N_2O, Si_3N_4 and SiC.[4–6] On pyrolysing the coked rice husk at 1400–1600°C, C and SiO_2 combine to give SiC, but some free C and SiO_2 remain as impurities. SiO_2 has to be removed by HF treatment and carbon by igniting at 600–650°C. On the other hand, formation of Si_2N_2O and Si_3N_4 was observed on pyrolysing the strong acid treated products under N_2 or NH_3 atmosphere at 1200–1400°C.

However, the whiskers thus formed have not fully characterised and the location of Si in the unreacted rice husk has been in doubt. The present work is devoted to defining the bonds and following their existence at elevated temperature by using IR spectroscopy. The small amount of SiO_2 and carbon remaining as contaminants on the surface could not be identified. But various types of bonding among Si, C and O have been distinguished according to their bonding energies. The sputtered surface and the internal surface could be analysed by XPS.

The mechanism for the development of whisker from oxide to oxynitride, nitride and carbide have been conceived as the same as the VLS mechanism in metals.[7] For the production of SiC from $(CH_3)_3SiCl$ or $(CH_3)_2SiCl_2$, H_2, CH_4 and CO are passed from external source, while in rice husk these gases are produced from the raw material itself[8] which is included to schematise the mechanism. Some additional information from the chemical analysis and DTA, TGA, IR, ESCA and XRD have confirmed the formation of whiskers from rice husk.

2 EXPERIMENTAL

Rice husk from Damanjodi in Orissa was coked to remove the oily substance at 300–400°C in a glass vessel and chemical treatment was done in a glass beaker, which after drying was transferred to a high alumina reactor. The mouth of the reactor was properly closed and then placed in a high temperature furnace for pyrolysis, N_2 or NH_3 gas

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was passed through the furnace of 0·2 dm^3 min^{-1}, and the temperature was gradually raised as per requirement at the rate of 5°C min^{-1}. The soaking temperature was maintained for a period of 4 h. After heat treatment the furnace was cooled to room temperature without stopping the flow of the gas.

The chemical analysis of trace elements was carried out in an atomic absorption spectrophotometer (model to 1435) and visible spectrophotometer (both from Varian). DTA or M/S Stanton REDCROFT was used. IR studies were conducted with KBr pellets in a Perkin-Elmer IR spectrophotometer. The X-ray photoelectron analysis was carried out in a Perkin–Elmer 570 AES/ESCA spectrometer. XRD of Phillips was used to determine the different phases present in the products.

3 RESULTS AND DISCUSSION

Chemical analysis of different parts of a paddy plant is shown in Table 1. The composition varies from place to place mainly due to the soil and nature of species since geographical conditions remain essentially the same. The rice husk is taken for study due to its availability and high percentage of SiO_2. Though the silica content is more in roots, it cannot be removed from the soil after harvesting of crop, because it is a main nutrient for the crop after its decomposition in the field by natural weathering. The chemical analysis of raw rice husk shows 74% of organic matter, composed of cellulose, lignin and hemi-cellulose. The hemicellulose is a mixture of *D*-xylose, *L*-arabinose, methyl glucoronic acid and *D*-galactose.[5]

3.1 Chemical treatment

On NaOH treatment, the SiO_2 is converted to Na_2SiO_3. Table 2 shows the effect of varying NaOH concentration at 100°C. The table indicates that an increased different percentage of SiO_2 is retained in rice husk with increased normality of NaOH. The calculated value of 6·15% tallies with the experimental value obtained at 9N. At concentrations below 9N, some amount of SiO_2 is also retained in rice husk (1–3%) which is assumed to be bonded with the monosaccharides.[9] This percentage varies, as the energies between silicon and the monosaccharides are different. The energy is released depending on the concentration of NaOH.

Table 1. Chemical analysis of different parts of a paddy plant

Constituent	Content (wt%)			
	Root	Husk	Straw	Leaf
Organic matter	54·80	73·70	83·89	89·35
SiO_2	40·50	21·87	12·42	6·96
Fe_2O_3	1·20	1·34	0·61	0·14
Al_2O_3	1·05	1·06	0·87	0·67
CaO	0·85	0·86	0·42	0·23
Na_2O	0·36	0·66	0·46	0·58
MgO	0·19	0·22	0·70	1·06
K_2O	0·29	0·18	0·24	0·37
MnO	0·05	0·06	0·07	0·16

Table 2. Treatment of rice husk with NaOH at 100°C

Normality of NaOH	SiO_2 (wt%)
1·0	2·051
2·0	2·068
3·0	2·097
5·0	3·115
7·0	5·741
9·0	6·670

3.2 Thermogravimetric analysis

Thermogravimetric analyses (TGA) of raw rice husk have been conducted in argon and air up to 900°C. Figure 1 indicates the weight loss against temperature curves of raw rice husk in argon and air. It can be seen that loss is significant at about 200°C, and the trend continues up to 500°C and remains constant at 550°C in the case of raw husk. It is surprising that the weight loss is higher in argon atmosphere than in air. The air surrounding the sample is contaminated with a reducing atmosphere due to the burning of carbon and therefore, the loss in this case is less than that

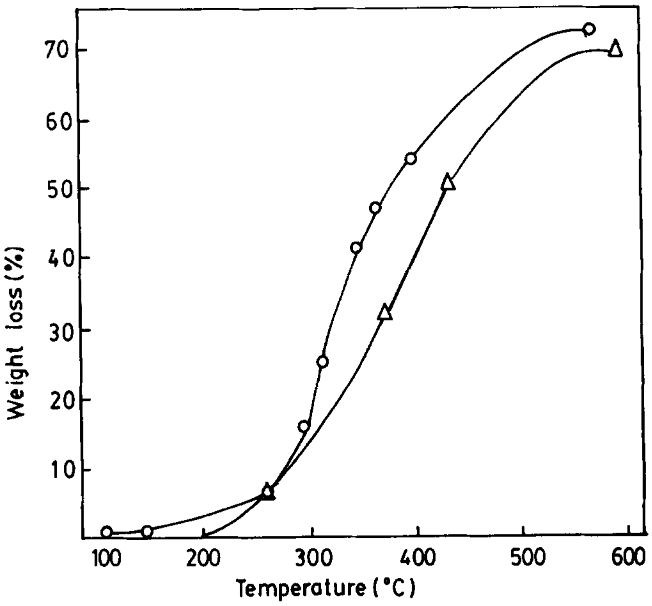

Fig. 1. TGA of rice husk [○ — argon, Δ — air].

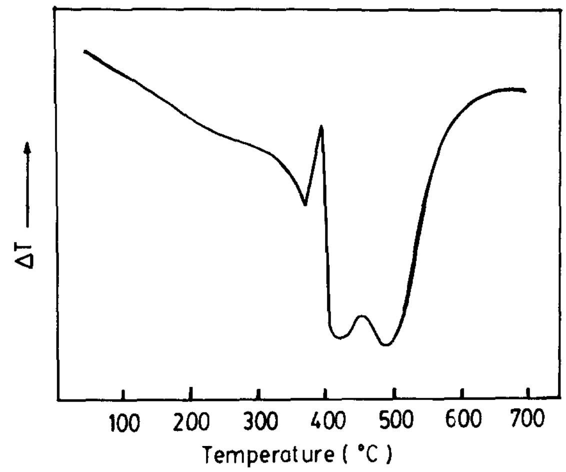

Fig. 2. DTA of rice husk.

in argon atmosphere. Beyond 600°C, the loss becomes insignificant and therefore, is not presented in this graph. The DTA curve of raw rice husk (Fig. 2) indicates a sharp exothermic peak at ~370°C followed by two other peaks at 400–500°C. The DTA peak at 370°C represents the decomposition of organic compounds. The next at 420°C may be attributed to decomposition of the cellulosic part and bonding of organic molecules with silicon atom in lignin of rice husk. The peak at 525°C is due to the transformation of α to β quartz.

3.3 *IR studies*

The presence of free SiO_2 indicated by peaks at 192, 196, 207, 218 and 468 cm^{-1} in raw rice husk is detected (Fig. 3). The peak at 1083 cm^{-1} is due to the SiO bond between Si^{4+} and O^{2-} of the carbohydrate molecules. The peak at higher wavelengths, near 3436 cm^{-1}, is due to hydroxyl groups. The peak at 800 cm^{-1} is considered to be the bonding between C and Si.

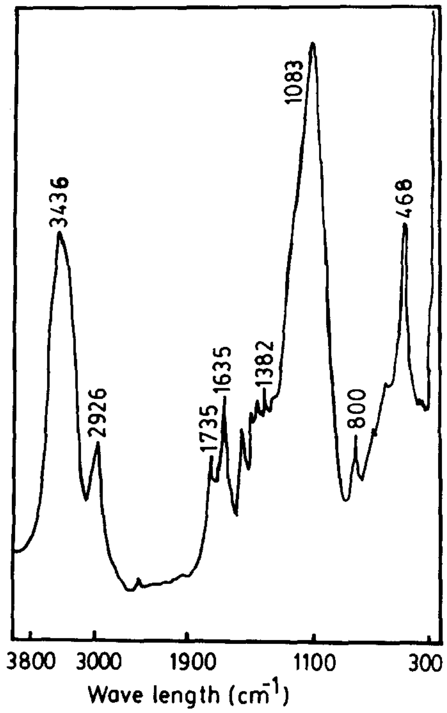

Fig. 3. IR spectra of raw rice husk.

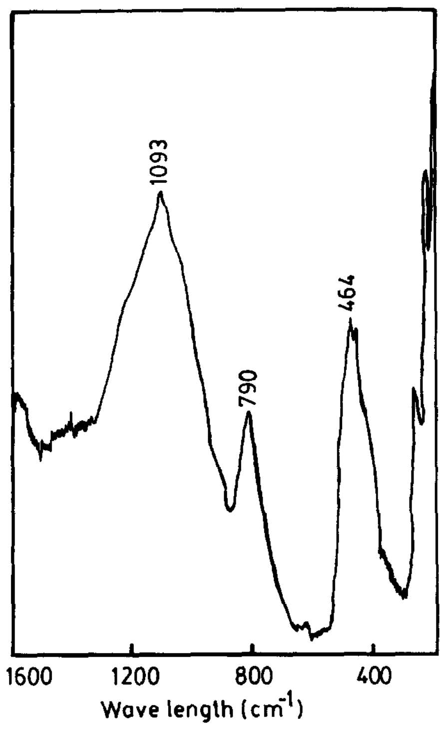

Fig. 4. IR spectra of coked husk.

In the IR spectra of rice husk after coking at 300°C for 4 h (Fig. 4), no peaks are obtained at higher wavelengths and therefore, the figure indicates the wavelengths up to 1600 cm^{-1}. All three peaks of rice husk are retained but the nature of the peaks at 464 and 1093 cm^{-1} changed slightly and the peak at 800 cm^{-1} moved to 790 cm^{-1}, thereby showing that the bond has become stronger with lower wavelength. The peak at 1099 cm^{-1} has become broad, unlike that for raw rice husk. This is due to the Si and O bonding, or from a combination of silica and carbohydrates.

It can be seen from Fig. 5 that the peak in the regions at 460 and 1080 cm^{-1} have disappeared with the development of two new peaks at 486 and 1122 cm^{-1}. It may be suggested that the peak at 486 cm^{-1} is due to SiO_2 and the one at 1122 cm^{-1} is due to SiC. The presence of a peak at 790 cm^{-1} is the same as in coked rice husk, which indicates that some SiC bonds remain present initially.

Unlike in the coked rice husk (Fig. 6) the product does not show any peak at 790 cm^{-1}. The peaks at 493 and 684 cm^{-1} show the bonding of silicon and nitrogen. The peak at 1089 cm^{-1} in rice husk has disappeared and Si^{4+} (of SiO) and NH_3 reacted to form Si_3N_4. The appearance of peaks at 850 and 933 cm^{-1} is due to the formation of Si_3N_4.

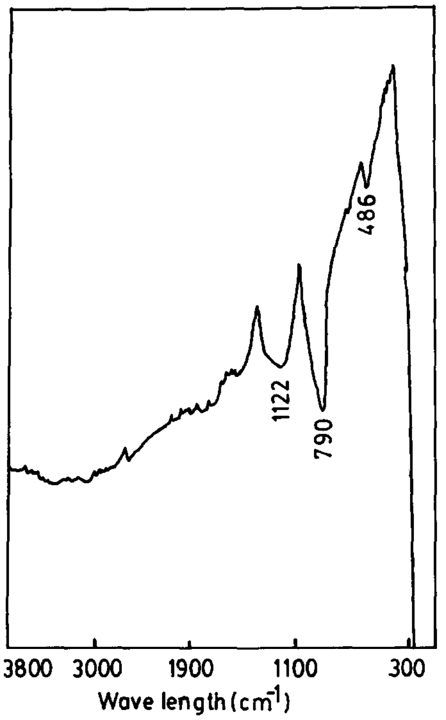

Fig. 5. IR spectra of SiC.

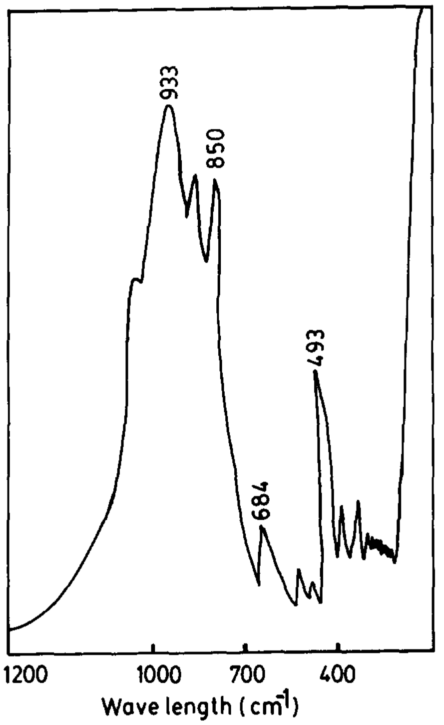

Fig. 6. IR spectra of Si_3N_4.

3.4 XPS studies

The X-ray photoelectronic spectra shows the presence of O, Si, F and C. Si present in the 2_s and 2_p levels accounts for 29% and C in the 1_s level accounts for 10.9%, assuming that all the carbon is bonded to Si in SiC (10·9% of C requires 25·49% of Si and the remaining 3·5% of Si should be bonded to oxygen (2%)). However, the O_2 level was 53·7%. The presence of such a large excess of O_2 (51·7) may be due to free O_2 and surface absorbed water molecules. Figures 7 and 8 show the spectra indicating the presence of Si (2_s and 2_p), C(1_s), O(2_s and 1_s) and F after removing 50 Å and 400 Å. Figures 9 and 10 represent the electronic spectra of SiC surface before and after sputtering to a depth of 50 Å. It can be confirmed by comparing these two figures that on sputtering, SiO_x decreases, whereas SiC increases, on the sputtered surface.

The Si spectra, as in Fig. 11, shows two bands, one at 105·31 and the other at 102·67, which change to three bands at 104·56, 103·18 and 101·13 eV on sputtering. The intensity, areas and

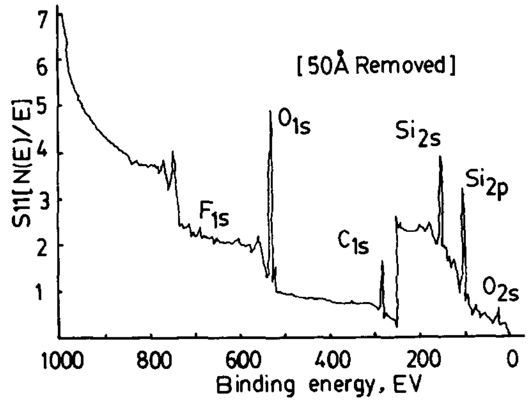

Fig. 7. Presence of different atoms in SiC.

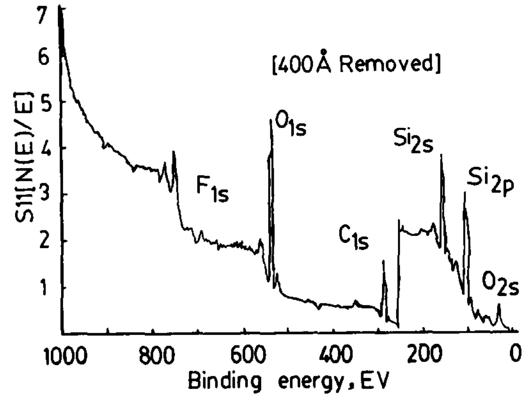

Fig. 8. Presence of different atoms in SiC.

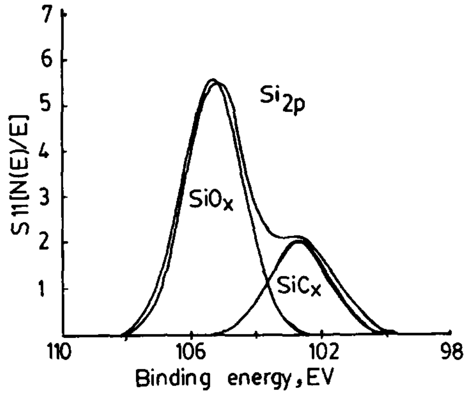

Fig. 9. Electron spectra of SiC.

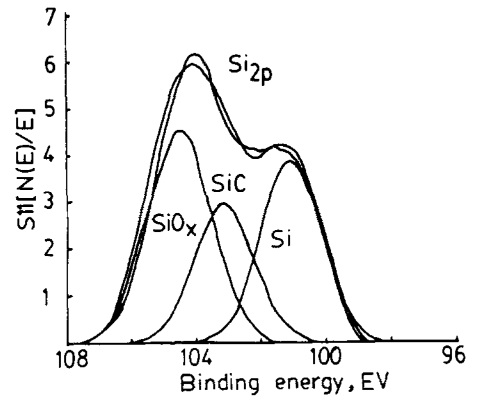

Fig. 10. Electron spectra of SiC (50Å removed).

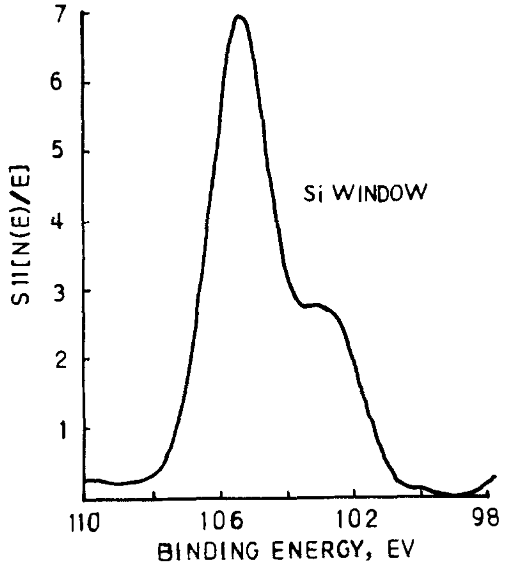

Fig. 11. Binding energy of Si in SiC.

peak positions of Si(2_p) and C(1_s) in solid SiC before and after sputtering of the surface, respectively, can be seen from Table 3. They differ from each other before and after sputtering of the SiC surface. The carbon spectrum is shown in Fig. 12 for the SiC surface. Figures 13 and 14 show the spectrum of O and F, respectively. The presence of F is due to contamination during removal of free SiO_3 by HF treatment. The O_2 peak is observed at 534·2eV on the SiC surface and at 533·65 eV in the sputtered sample, the drift being 0·55 eV. The corresponding peaks for F are at 687·8 and 686·9 eV, the latter having a dichoric character.

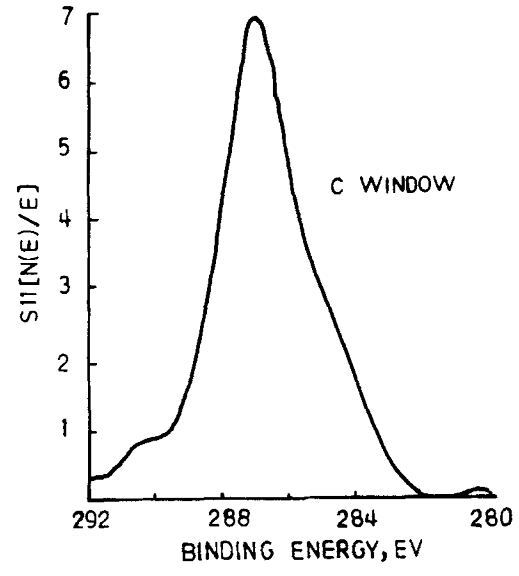

Fig. 12. Binding energy of C in SiC.

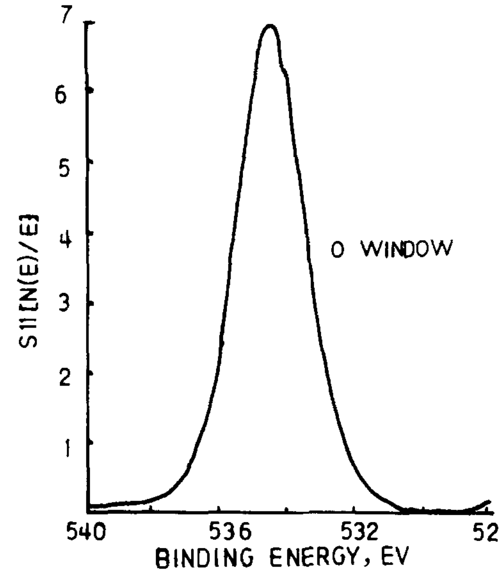

Fig. 13. Binding energy of O in SiC.

3.5 XRD studies

The XRD of rice husk ash and the different products obtained at various temperatures are presented here. The formation of trydimite is confirmed from Fig. 15(a) after pyrolysing the rice husk at 1250°C. The XRD of the products obtained at 1600°C are essentially a mixture of cristobalite,

Table 3. X-ray photoelectron analysis of SiC solid surface

	Si (2_p)					C (1_s)						
	Before sputtering		After sputtering of 50 Å			Before sputtering			After sputtering of 50 Å			
Bands	I	II	I	II	III	I	II	III	I	II	III	IV
Peak position	105·11	102·6	104·46	103·11	101·15	289·73	287·17	284·95	286·80	285·22	283·65	288·35
Intensity	1618	618	890	588	774	221	2235	731	770	1230	988	71
Area	3703	1390	2211	1383	1799	515	5342	1699	1810	4520	2316	144

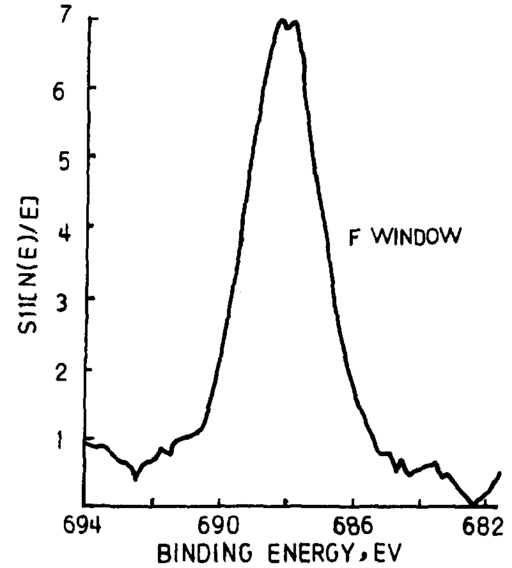

Fig. 14. Binding energy of F in SiC.

trydimite and SiC, as can be seen from the *d*-values (Fig. 15(b)). The presence of cristobalite is confirmed from the *d*-values of 2·86, 3·15 and 4·07 and *d*-values of 3·35 and 3·60 are due to trydimite. The *d*-values of 1·30, 1·53, 2·16 and 2·50 are due to SiC. The progress of SiC formation is confirmed by an increase in the peak height corresponding to the *d*-value at 2·51 and the decrease of peak height corresponding to the *d*-value of 4·10, which is for trydimite. Figure 15(c) shows the XRD of the product obtained at 1600°C after HF treatment and then ignition at 525°C. From the *d*-values it is confirmed that the product is SiC. It is interesting to note that the SiC formation takes place without the addition of a catalyst from an external source. Of course, rice husk itself contains the metal ions which act as catalysts.

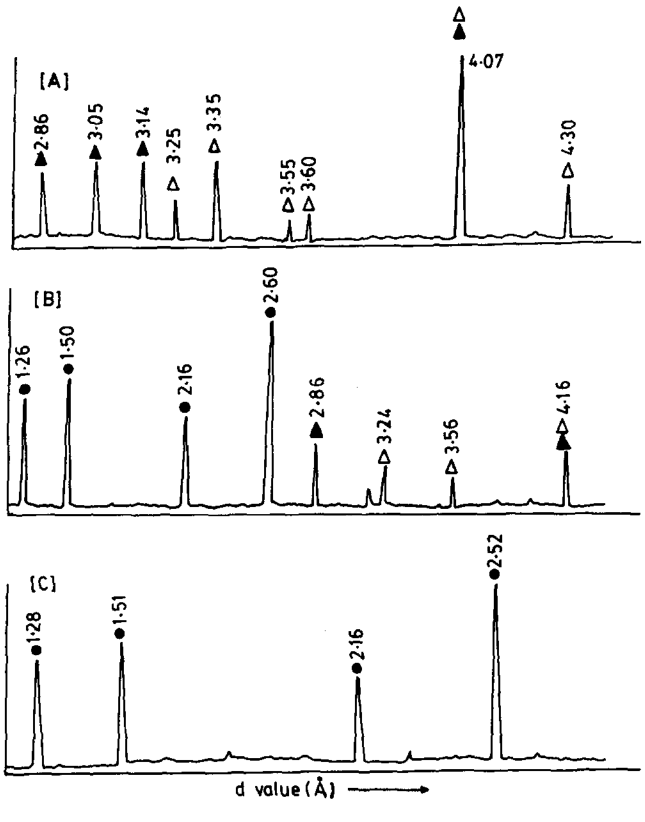

Fig. 15. X-Ray diffractogram of products during formation of SiC. (A) Rice husk pyrolysed at 1250°C; (B) product obtained at 1600°C; (C) HF treatment of (B) [● — SiC, Δ — tridymite, ▲ — cristobalite].

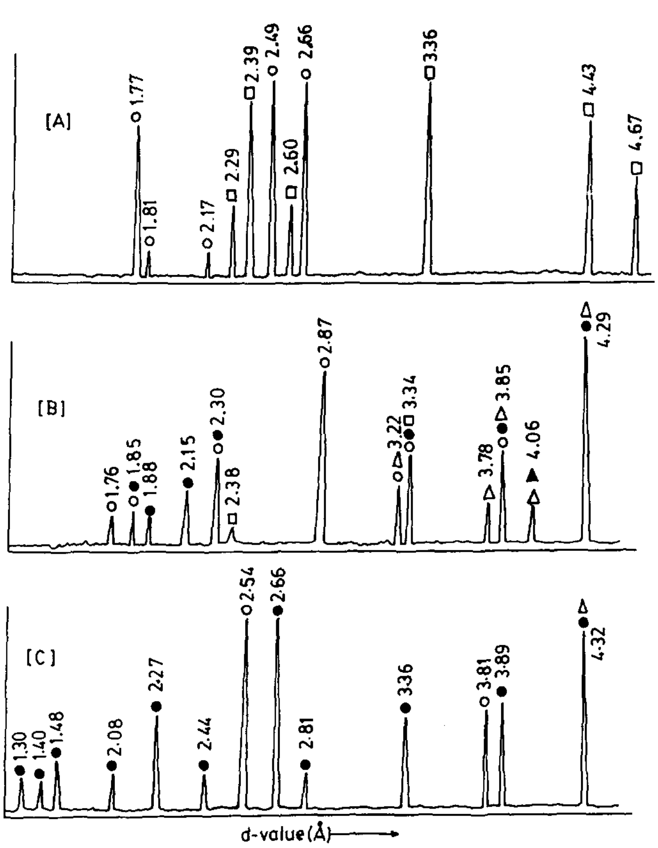

Fig. 16. X-Ray diffractogram of Si_3N_4 and Si_2N_2O. (A) In N_2 and NH_3 atmosphere at 1300°C; (B) in NH_3 atmosphere at 1300°C; (C) (B) at 1400°C [● — α-Si_3N_4, O — β-Si_3N_4, □ — Si_2N_2O, Δ — tridymite, ▲ — cristobalite].

Typical X-ray diffractrograms of the products obtained from acid treated rice husk under N_2 and NH_3 atmospheres showing the presence of Si_2N_2O and Si_3N_4 are presented in Fig. 16(a) where both the phases exist. The presence of a second phase cannot be ignored as *d*-values in A at 2·49 and 2·66 are quite distinct. The phase is recognised by the appearance of most of the *d*-values, including those at 1·48, 2·54, 2·60 and 2·88 (Fig. 16(c)) which represent some intense reflection of Si_3N_4 phase. It is surprising, however, that Si_3N_4 can be obtained even without addition of catalyst. Figure 16(b) and (c) show the products obtained at 1300 and 1400°C, respectively, under NH_3 atmosphere. Si_2N_3O also appears along with Si_3N_4 at 1300 and 1400°C.

3.6 Chemical analysis of products

Metals have been reported to act as catalysts in the formation of alumina whisker and therefore analysis of the metallic elements present at every stage of heat treatment producing SiC, Si_2N_2O and Si_3N_4 needs to be thoroughly evaluated. The results for trace elements present in the products are tabulated in Tables 4, 5 and 6. The seven elements detected are: Al, Fe, Na, K, Ca, Mg and Mn. The elements are expressed as their respective oxides. It is possible to obtain these ceramic materials without addition of any metal catalysts from external sources. It is certain that the metals present initially serve this purpose if they participate at all in ceramic materials. Oxides such as Na_2O, K_2O, CaO and MgO can, on the other hand, impart a fluxing effect. These are also present above 1400°C. It is therefore established that the ceramic material can be formed without catalyst from external source,[10] considered as indispensible.

Table 4. Chemical analysis of SiC obtained at different temperatures

Constituent	Temperature (°C) 1400	 1500 Content (wt%)	 1600
Free C	1·90	1·00	0·50
SiO_2 (Free)	1·00	0·80	0·70
Al_2O_3	0·26	0·27	0·27
Fe_2O_3	0·23	0·23	0·23
CaO	0·18	0·19	0·19
MgO	0·04	0·04	0·04
Na_2O	0·06	0·04	0·02
K_2O	0·05	0·04	0·03
MnO	0·011	0·012	0·012
V_2O_5	0·001	0·001	0·001
SiC	96·2	97·3	97·9

Table 5. Chemical analysis of Si_3N_4 obtained at different temperatures

Constituent	Temperature (°C) 1200	 1300 Content (wt%)	 1400
Free C	0·39	0·27	0·18
SiO_2 (Free)	0·65	0·35	0·30
N	39·76	39·54	39·50
Al_2O_3	0·30	0·36	0·47
Fe_2O_3	0·17	0·14	0·10
CaO	0·127	0·138	0·138
MgO	0·09	0·10	0·12
Na_2O	0·002	0·001	0·001
K_2O	0·002	0·001	0·001
MnO	0·011	0·012	0·012
V_2O_5	0·001	0·001	0·001

Table 6. Chemical analysis of Si_2N_2O obtained at different temperatures

Constituent	Temperature (°C) 1200	 1300 Content (wt%)	 1400
Free C	0·40	0·32	0·30
SiO_2 (Free)	0·70	0·60	0·55
N	28·9	28·5	28·3
Al_2O_3	0·36	0·34	0·30
Fe_2O_3	0·20	0·18	0·17
CaO	0·13	0·14	0·14
MgO	0·13	0·14	0·14
Na_2O	0·003	0·002	0·002
K_2O	0·002	0·002	0·002
MnO	0·011	0·011	0.011
V_2O_5	0·001	0·001	0·001

3.7 Mechanism of formation

The formation of SiC from rice husk has been explained by carbothermal reduction according to the reactions (1–5) of SiO_2 with carbon, which are the major constituent of rice husk.

$$SiO_2 + 2C = SiC + CO_2 \tag{1}$$
$$SiO_2 + 3C = SiC + 2CO \tag{2}$$
$$SiO_2 + C = SiO + Co \tag{3}$$
$$SiO + C = Si + CO \tag{4}$$
$$2Si + 2CO = 2SiC + O_2 \tag{5}$$
$$2C + O_2 = 2CO \tag{6}$$
$$2NH_3 = N_2 + 3H_2 \tag{7}$$
$$SiO_2 + H_2 = SiO + H_2O \tag{8}$$
$$SiO + H_2 = Si + H_2O \tag{9}$$
$$3Si + 2N_2 = Si_3N_4 \tag{10}$$
$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO \tag{11}$$
$$3SiO_2 + 2N_2 = Si_3N_4 + 3O_2 \tag{12}$$
$$2H_2O = 2H_2 + O_2 \tag{13}$$
$$Si_3N_4 + O_2 = Si_2N_2O + SiN_2O \tag{14}$$
$$SiN_2O + Si = Si_2N_2O \tag{15}$$
$$2Si_2N_2O + 4CO = 4SiC + 4NO + O_2 \tag{16}$$
$$SiN_2O + CO = SiC + 2NO \tag{17}$$
$$2NO + O_2 = 2NO_2 \tag{18}$$

In the present work N_2 and NH_3 atmospheres have been employed for production of these ceramic materials. However, in the above reactions which have a justification to be well accepted, the participation of carbon seems to be difficult. As an atmosphere of N_2 or NH_3 facilitates a number of reaction steps, it could be conceived that the gas molecules, like H_2, O_2, N_2 and CO, can participate during the formation of products. At elevated temperature, NH_3 dissociates to N_2 and H_2 (eqn (7)). The latter, being a highly reducing agent, could be able to reduce SiO_2 in two steps, as shown in eqns (8) and (9), to metallic Si which can react spontaneously with N_2 to form Si_3N_4 (eqn (10)). During the reaction process the transformation of Si_3N_4 to Si_2N_2O is by oxidation after dissociation of water molecules, formed after reduction of SiO_2 to Si (eqn (9)). The formation of SiC from Si_2N_2O can be explained from eqns (14)–(17). The oxygen molecule, which is produced after dissociation of a water molecule, oxidises Si_3N_4 to SiN_2O and Si_2N_2O. SiC and NO can be formed when CO reacts with SiN_2O

and Si_2N_2O. NO which is produced according to eqns (16) and (17) oxidises to NO_2 as per eqn (18). This information also allows for a more certain prediction for the reaction mechanism of the formation of SiC, Si_3N_4 and Si_2N_2O from rice husk through a complicated process unlike metals.

4 CONCLUSIONS

Rice husk possesses significant non-degradable portions on treatment with NaOH and thermal treatment. The amount of SiO_2 retained in rice husk is 5·3% and after alkali treatment to heat treated (1000–1250°C) rice husk, 3–7% of SiO_2 remained as non-reactive. The IR studies show the bonding of SiO_2 with C and N_2 in the raw materials, intermediate and final products. The XPS analysis shows the bonding of O_2, C and Si, as well as the free SiO_2 in the products before and after sputtering. The presence of different phases are determined with the help of XRD. The trace elemental analysis shows the metallic elements present in rice husk which can participate in reaction without adding catalysts from any external source. However, the formation of SiC, Si_2N_2O and Si_3N_4 can be explained through the proposed mechanism.

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