

Studies on the Formation of Silicon Nitride and Silicon Carbide from Rice Husk

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ABSTRACT

Rice husk is a potentially useful source material for the production of silicon nitride, silicon carbide or a mixture of both. Pyrolysis of rice husk yields an intimate and homogeneous mixture of carbon and silica which is highly desirable for a good carbonitrothermic or carbothermic reduction process. The formation of Si_3N_4 occurs on heating the pyrolysed rice husk to 1400°C under nitrogen flow and SiC forms in the presence of excess carbon at temperatures above 1450°C . SEM and XRD results show that the morphology of the nitride product is influenced by the reaction temperature and the presence of additives.

1. INTRODUCTION

Silicon nitride has attractive technological properties like high temperature oxidation resistance, low density, high hardness, high strength and resistance to thermal shock. It has therefore been considered for use in high temperature turbine components, bearings and cutting tools. The applications of Si_3N_4 are, however, limited by its poor fracture toughness. The dispersion of SiC in Si_3N_4 matrix is known to increase the strength and fracture toughness of the composite /1,2/. The properties of the composites, however, depend on the morphology, chemical composition and particle size of the initial powder which are influenced by methods used for their preparation. There are many routes for the production

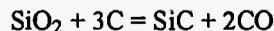
of silicon nitride /3/. They include synthesis by nitridation of elemental silicon, reaction of silicon chloride with ammonia, and reduction nitridation of silica. The reduction nitridation of silica, which is also called carbonitrothermic reduction as it involves carbothermic reduction under a nitrogen atmosphere, can also be used to prepare silicon nitride – silicon carbide mixtures. Other methods for preparing SiC/ Si_3N_4 composite powders include gas phase synthesis of fine amorphous Si-C-N particles from $\{(\text{CH}_3)_3\text{Si}\}_2\text{NH}$ /4/ and from $\text{SiH}_4\text{-CH}_3\text{-NH}_2$ or $\text{SiH}_4\text{-C}_2\text{H}_2\text{-NH}_3$ /5/. Among the various methods, the preparation of silicon nitride or the nitride-carbide composite by the carbothermic reduction-nitridation of silica is considered attractive as the method yields pure nitride or composite of fine particle size from inexpensive raw materials. In this context rice husk is a useful raw material because it contains both carbon and silica. Besides, silica and carbon are present in rice husk as an intimate and uniform mixture.

2. THEORETICAL CONSIDERATIONS

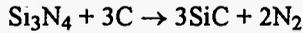
The overall reaction for the formation of silicon nitride from silica can be represented by



and the formation of silicon carbide by



Silicon nitride can be transformed into silicon carbide, in the presence of carbon, by



The temperature at which each of these reactions occurs depends on the free energies of formation of SiO_2 , CO , SiC , and Si_3N_4 , as well as on the partial pressures of N_2 and CO in the system. These details have been presented by Ishi *et al.* /6/ in a diagram shown in Fig. 1.

The minimum temperature at which a $\text{SiO}_2 + \text{C}$ mixture can be converted to Si_3N_4 or SiC , at $p_{\text{CO}} = 0.01$ atm, is $\sim 1200^\circ\text{C}$. If the p_{CO} value is higher, the carbide or nitride can be formed only at high temperatures. At 1500°C , the silica-carbon mixture converts to the silicon carbide-carbon mixture or silicon nitride-carbon mixture at $p_{\text{CO}} = 1$ atm. Whether the nitride forms or the carbide forms is determined by the partial pressure of nitrogen. At a given temperature and p_{CO} value, the carbide formation is favoured at low nitrogen pressures and nitride formation is favoured at

higher nitrogen pressures. Above about 1475°C , for nitride to form the required partial pressure of nitrogen is more than 1 atm; the required minimum partial pressure of nitrogen increases with further increase in temperature. An experimental arrangement involving nitrogen flow over a silica-carbon mixture at a temperature in the range of 1350 to 1500°C can provide a low value of p_{CO} and a high value of p_{N_2} . The product that can be anticipated on the basis of this diagram is pure nitride at low temperatures and an increasing amount of carbide at higher temperatures.

3. EXPERIMENTAL DETAILS

The rice husk used in this investigation was obtained from the Trakya region in Turkey. The husk was washed with deionised water and dried at 100°C for 3h. The dried husk was pyrolysed under argon flow at 700°C for 1h and ground in a WC vibratory mill. The chemical analysis of the pyrolysed rice husk (PRH) is given in Table 1. The surface area of the pyrolysed rice husk was $150 \text{ m}^2\text{g}^{-1}$. The X-ray analysis by the Scanning Electron Microscope revealed that the concentration of Si is slightly higher at the outskirts of the rice husk particles than in the interior portions. The PRH powder was formed into 3-4 mm diameter pellets by moistening before loading into the reactor.

In another set of experiments, Si_3N_4 powder having a BET value of $11.5 \text{ m}^2\text{g}^{-1}$ was used as the nucleation agent. The nitride powder was added to the PRH before carbonitrothermic-reduction.

The carbothermic reduction and nitriding experiments were carried out in a graphite resistance furnace (Tammann 44 kVA, max 2500°C) using a specially designed graphite chamber. A Pt-Pt10Rh thermocouple was used for temperature measurement. Nitrogen gas was passed through copper turnings kept at 500°C to bring down the oxygen content to below 0.1 ppm before it entered the reactor.

The carbothermic reduction and nitridation experiments were carried out by placing about 5g of charge in the reactor and heating it at 1350 to 1500°C for up to 6h under 50 l h^{-1} nitrogen flow. After nitridation, excess carbon in the product was burnt off

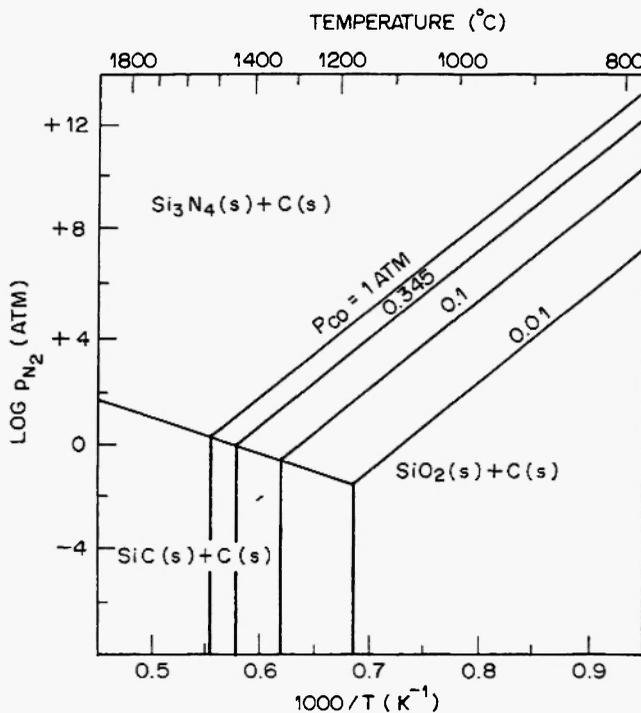


Fig. 1: Thermochemical correlation for stability of Si_3N_4 , SiO_2 and SiC under coexistence with carbon /6/.

Table 1
The chemical composition of pyrolysed rice husk
(PRH) powder

Component	Composition, wt%
SiO ₂	47.91
Fe ₂ O ₃	0.701
MnO	0.102
Na ₂ O	0.161
K ₂ O	0.256
CaO	0.174
MgO	0.270
C	50.0

in air at 700°C for 3h and then the unreacted silica in the product was removed as sodium silicate by boiling in sodium hydroxide solution (20 wt%) for 20min. The crystalline phase composition of the reaction product was analysed using an X-ray diffractometer with CuK α radiation. The morphology of the product was determined by Scanning Electron Microscopy.

4. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the products obtained after nitriding at 1350, 1400, 1450 and 1500°C for 2h are shown in Fig. 2. α -Si₃N₄ phase was

detected at temperatures 1350, 1400 and 1450°C but was not found at 1500°C. The amount of α -Si₃N₄ increased with increase in temperature and reached a maximum at 1400°C. At this temperature, the amount of Si₃N₄ formed increased gradually up to 2h of reaction time and started to level off afterwards. The formation of SiC phase was first observed at 1450°C. At 1500°C it was the major phase and no Si₃N₄ was observed.

The effects of temperature and time on the formation of Si₃N₄ are shown in Fig. 3. The relative amount of silicon nitride formed was determined from the area under the XRD peak. At 1350°C, the percentage of Si₃N₄ formation increases with an

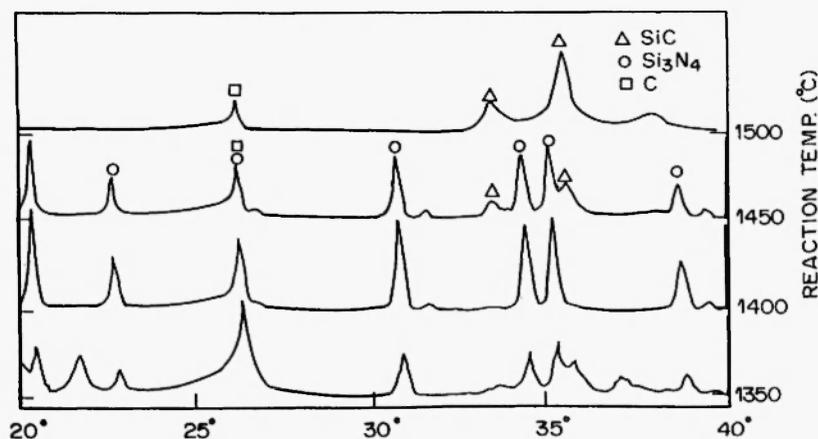


Fig. 2: XRD results of nitridation experiments after 2 h of reaction at several temperatures.

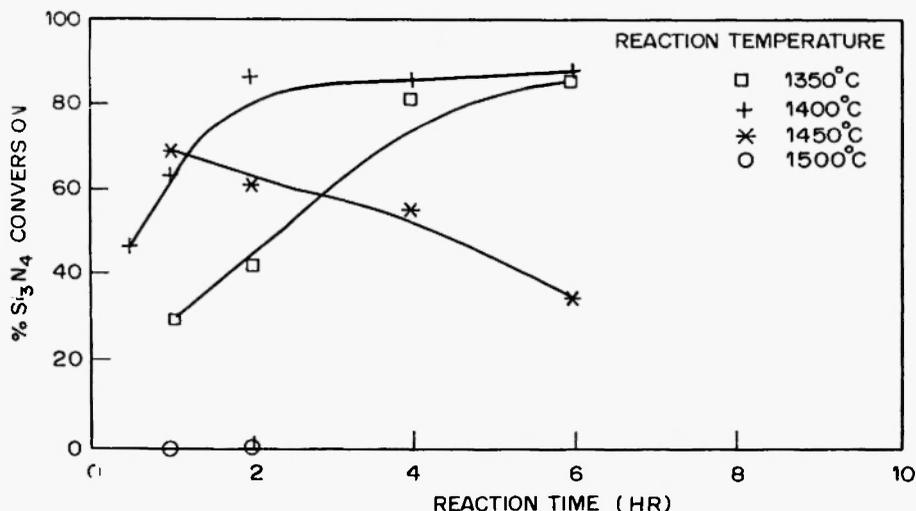
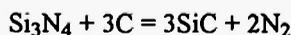


Fig. 3: The effect of reaction temperature and time on nitridation of PRH powder.

increase in reaction time, reaching the maximum value of about 85% in 6h. Increase in temperature to 1400°C markedly increases the speed of conversion resulting in ~85% silicon nitride formation in only 2h. At 1450°C, however, more Si₃N₄ forms (than at 1400°C) in the first hour but it soon begins to convert to SiC, the extent of conversion to SiC increasing with reaction time up to 6h. At 1500°C, no Si₃N₄ formation was observed up to 2h of reaction time.

The product of carbonitrothermic reaction of PRH powder is Si₃N₄ at 1400°C, a mixture of Si₃N₄ and SiC at 1450°C and only SiC at 1500°C. At 1450°C, the proportions of the carbide and the nitride in the product depend strongly on the reaction time. This is shown in Fig. 4. The conversion of Si₃N₄ to SiC increases slowly at first, up to 4h of reaction time, but the increase is rather sharp between 4h and 6h of reaction time. Excess carbon, which is a necessary component in the carbonitrothermic production of silicon nitride, brings about the decomposition of Si₃N₄, which may be represented as



The free energy of this reaction is -3kJ at 1450°C. Besides, iron present in the PRH powder plays a catalytic role in the formation of SiC above about 1450°C.

In the carbothermic reduction of PRH, it was

observed that the Si₃N₄ product is obtained in the form of whiskers. The graphite reactor interior as well as the charge surface were covered with Si₃N₄ whiskers. The whisker morphology was found to be different depending on the temperature of reaction. The reaction at 1450°C yielded whiskers with some spherical globules at their tips, while the whiskers formed at 1400°C did not have such globules. XRD analysis of the whiskers showed the presence of only Si₃N₄ in each case. The light element energy dispersion X-ray analysis, taken from a whisker containing globules, indicated the presence of the elements silicon and nitrogen, confirming the XRD results. X-ray mapping of the globules displayed the presence of Fe, C and Si which could form a low melting liquid phase during the nitridation reaction which results in the formation of Si₃N₄. Two mechanisms have been proposed to explain the whisker formation in carbonitrothermic silicon nitride preparation: the vapour-solid (V-S) mechanism /7/ and the vapour-liquid-solid (V-L-S) mechanism /8/. The V-S mechanism operates at the lower temperatures (1400°C in the present case) and results in the formation of whiskers with no globules. The V-L-S mechanism dominates the whisker formation above 1400°C and results in the formation of whiskers with globules.

The morphology of Si₃N₄ product obtained by carbonitrothermic reduction of PRH could be changed by using additives. In experiments where Si₃N₄ powder

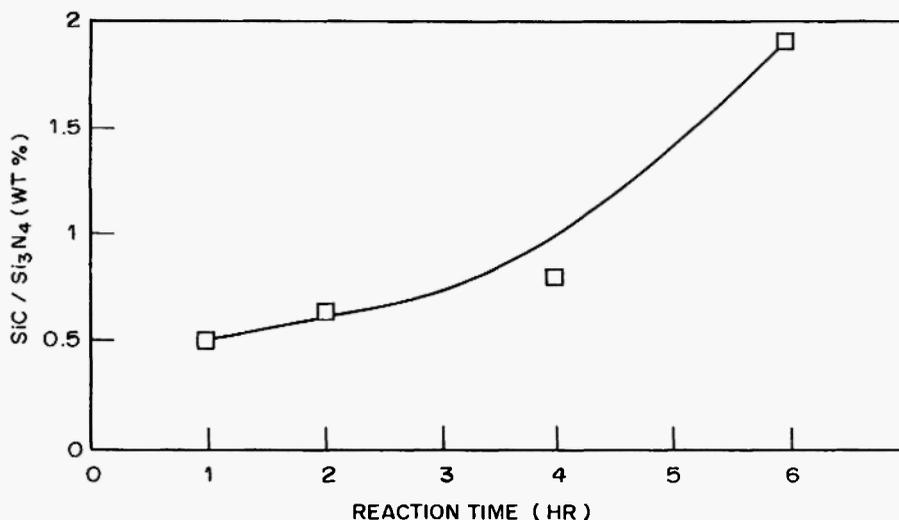


Fig. 4: The effect of reaction time on the proportions of SiC and Si₃N₄ in the product of carbonitrothermic reduction of PRH at 1450°C.

(having 11.5 m²g⁻¹ BET value) was added to PRH powder before carbonitrothermic reduction the product morphology was equiaxed grains. The nitride additive has functioned as seed for nucleation and brought about the change in the product morphology.

5. CONCLUSION

Pyrolysed rice husk contains both silica and carbon as an intimate and homogeneous mixture. It is a useful starting material for the preparation of silicon nitride as well as silicon nitride-silicon carbide mixture by a carbonitrothermic reduction reaction.

Carbonitrothermic reduction at 1400°C for 2 h yields α-Si₃N₄. At 1450°C the product contains both Si₃N₄ and SiC, the proportion of SiC increasing with increase in reaction time. At 1500°C only SiC is found in the product. The nitride product is obtained in the form of whiskers. The product morphology is different, equiaxial grains, if Si₃N₄ powder is added to PRH before carbonitrothermic reduction.

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