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The Formation of Different Si_3N_4 Phases in the Presence of V_2O_5 During Carbothermal Reduction of Untreated and Acid Treated Rice Husk

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Abstract: Silicon nitride with different phases was prepared by nitriding undigested and digested rice husk at 1430°C, under flowing nitrogen gas, in the present of V_2O_5 as catalyst. It was found that β-Si_3N_4 was the predominant phase in the product obtained from nitridation of undigested rice husk that containing excess of carbon ($C/SiO_2 = 7$). Meanwhile, Si_2ON_2 constitutes the major phase of the powder obtained from nitridation of digested husk which contains carbon and silica in a stoichiometric ratio of the overall reaction. However, both the undigested and digested husk produced α-Si_3N_4 when nitridation was carried in the absence of V_2O_5. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

INTRODUCTION

The overall reaction for carbothermal reduction and nitridation of rice husk can be written as

$$3SiO_2(s) + 6C(s) + 2N_2(g) = Si_3N_4(s) + 6CO(g) \quad (1)$$

The reaction involves silica and carbon in solid forms, but the actual mechanism as generally agreed is that Si_3N_4 forms through vapour phase in a complicated reaction sequences.[1–3]

The overall reaction is influenced by many factors such as characteristics of starting materials, temperature, gas flowrate and catalysts, which were reported by several researchers.[2,4,5] However, studies on the effect of V_2O_5 on the formation of β-Si_3N_4 is limited. In the authors' previous work,[6] it was reported that β-Si_3N_4 was formed during nitridation of rice husk in the presence of 2% V_2O_5. The present work reports the extension of the studies on the effects of V_2O_5 as catalyst for producing β-Si_3N_4 at a lower temperature as compared to those employing iron catalyst.[2] The effect of stoichiometry, carbon–silica molar ratio, during the formation of silicon nitride is also reported.

EXPERIMENTAL

Rice husk was washed with diluted HNO_3 (~1 M), filtered and repeatedly washed with distilled water, and dried. The dried husk was pyrolysed at 800°C for 1 h under flowing argon. The pyrolysed husk was ball-milled to provide the starting powder for nitridation. The content of silica and carbon was estimated by heating pyrolysed rice husk powder in air at 700°C for 1 h. Vanadium pentoxide (98.5%, BDH Chemical) was incorporated into pyrolysed powder by wet mixing for 2 h, and dried in a hot plate.

The sample (~2 g) in an alumina boat was placed in a controlled atmosphere furnace, and was heated in a controlled rate up to 1430°C for 2–6 h under flowing nitrogen gas (12.5 ml s^{-1}) at 1 atm pressure. After nitridation, the product was burned in air at 700°C for 30 min to remove any excess carbon.

The phases composition of the products was determined by X-ray diffraction (Siemens D5000). Morphology of the products was examined by scanning electron microscope (Stereoscan S500, and Cambridge S360).

Another set of experiments was performed by using digested rice husk as starting material. The husk was digested in 12 M HNO_3 for 3 h as described in detail elsewhere.[7] Further treatments of the samples followed the same procedure as described above.

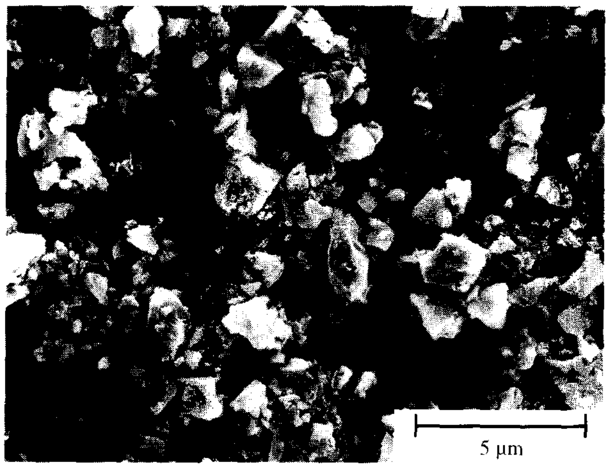
RESULTS AND DISCUSSION

Starting materials

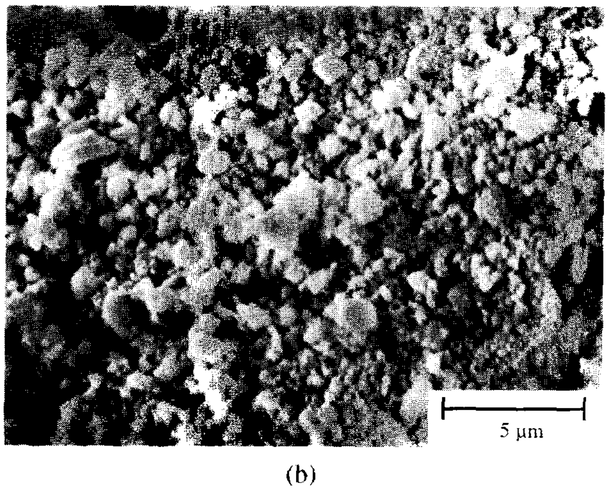
Scanning electron micrographs of undigested, and HNO_3 digested rice husk powder after pyrolysed at 800°C under flowing argon are shown in Fig. 1. Overall, the particle size of the undigested husk is irregular and the distribution is not homogeneous as compared to digested husk. Table 1 shows the C/SiO_2 molar ratio of the pyrolysed husks. The pyrolysed raw husk produced a starting material containing carbon and silica molar ratio of 7. After treating rice husk with 12 M, HNO_3 at 60°C for 3 h, the carbon and silica content of the pyrolysed husk was reduced to 2, that is, stoichiometric molar ratio of the overall reaction for carbothermal reduction.

Table 1. C/SiO_2 **molar ratio of pyrolysed rice husk at 800°C under flowing argon atmosphere**

Sample	Content(%) Carbon	Silica	C/SiO_2 Molar ratio
Undigested husk (Raw husk)	58	42	7
Digested husk (12 M HNO_3, 3 h)	29	31	2



(a)



(b)

Fig. 1. Scanning electron micrographs of the pyrolysed rice husk powders, (a) undigested husk, and (b) digested husk.

Nitridation of undigested rice husk

Nitridation of rice husk is, in principle, identical to the carbothermal reduction and nitridation of carbon and silica mixture (eqn (1)). The process has been reviewed through different mechanisms with different paths of reactions. However, the general opinion seem to be that SiO gas plays an important role in Si_3N_4 formation. Our authors' previous work[6,7] suggested that SiO(g) was generated by the reaction between SiO_2 and C (eqn (2)) due to the naturally mixed of the both reactants presence in rice husk:

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \qquad (2)$$

The subsequent reaction is

$$SiO(g) + 2/3N_2(g) = 1/3Si_3N_4(s) + 1/2O_2(g) \qquad (3)$$

The equilibrium partial pressure of oxygen associated with eqn (3) is calculated to be 3.3×10^{-10} Pa. In order for the reaction to proceed without the formation of silicon oxynitride, Si_2ON_2, oxygen must effectively be removed from the system by eqn (4).

$$1/2O_2(g) + C(s) = CO(g) \qquad (4)$$

This is not difficult since eqn (4) is thermodynamically favourable. K_p of eqn (4) at 1430°C is 1.1×10^8. Equations (3) and (4) proceed simultaneously which constitute a composite, eqn (5):

$$SiO(g) + C(s) + 2/3N_2(g) = 1/3Si_3N_4(s) + CO(g) \quad (5)$$

Thus, it is believed that the formation of α-Si_3N_4 may be nucleated and grown on the rice husk particles through eqn (5). The formation of silicon oxynitride can be eliminated as long as carbon is present in excess or at least in the stoichiometric ratio of the overall carbothermal reduction[8].

The scanning electron micrographs of the powder obtained from nitridation of undigested rice husk, as in Fig. 2(a) shows that Si_3N_4 powder consisted of hexagonal cross-section particles with about 1.3 µm in length. The morphology which is completely different from that of rice husk is attributed to α-Si_3N_4 is being the major product formed through a vapour phase reaction. The irregularity of the crystal shape indicates that may be associated with the view that eqn (5) is the most likely the growth reaction for this system.

Most of the works[1,4,6,7] on the preparation of Si_3N_4 powders by carbothermal reduction process reported α-phase as the major phase, in belief that α–β transformation led to complete densification.[9] However, Lee *et al.*[10] proved that a dense body could be obtained during densification of β-phase powder. Sajgalik[11] reported that higher content of β-Si_3N_4 phase in the starting powder resulted in a higher rate of α–β transformation in the system reaction without sintering aids. This initiate several researchers to investigate the possibility of producing β-Si_3N_4, for example, by carbothermal reduction. Recently, it was reported[2] that Si_3N_4 powder with a predominant β-phase was produced from a fine silica–carbon mixture at 1540°C, in the presence of iron as catalyst. Below this temperature, a mixture of β-Si_3N_4, SiC and Si_2ON_2 was formed.

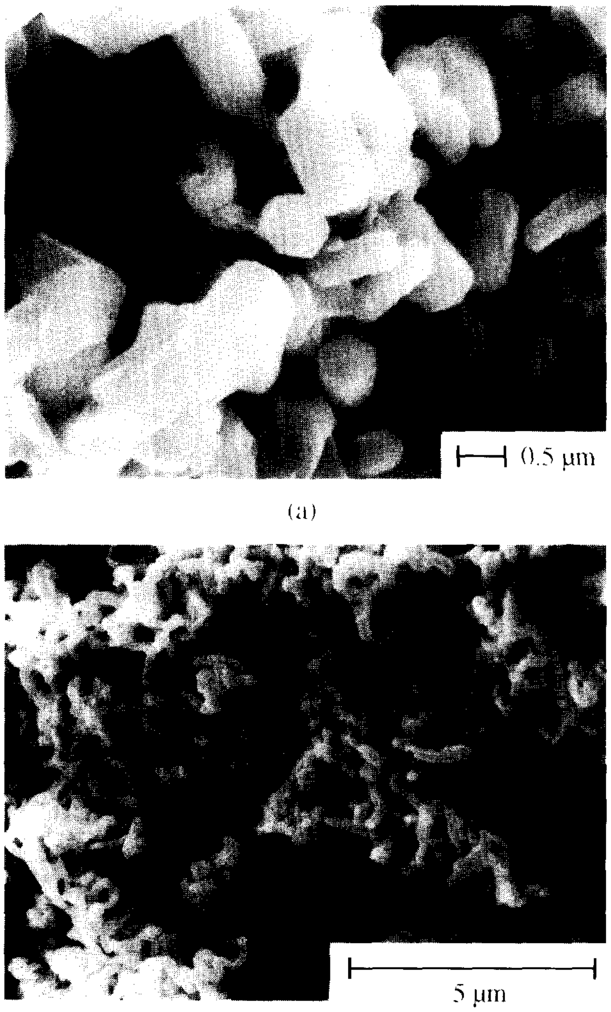


Fig. 2. Scanning electron micrographs of Si_3N_4 powders obtained from nitridation of pyrolysed rice husk. (a) Undigested husk; (b) undigested husk + 2% V_2O_5.

In this work, β-Si_3N_4 powder was prepared from rice husk which was incorporated with V_2O_5. The powder was prepared by nitridation of pyrolysed rice husk powder at 1430°C, which is 100°C lower than reported by Bandyopadyay *et al.*[2]

XRD analysis shown in Fig. 3 indicates a high percentage of β-Si_3N_4 in the products. The amount of β-Si_3N_4 increased significantly with V_2O_5 content, reaching a maximum of ~80% at 10% oxide, before decreasing again. VC and VN were detected as by-products, presumably to be formed through eqns (6) and (7), respectively:

$$V_2O_5(l) + 7C(s) = 2VC + 5CO \qquad (6)$$

$$V_2O_5(l) + 5C(s) + N_2(g) = 2VN(s) + 5CO(g) \qquad (7)$$

In all cases, VC was found to be the predominant phase due to its greater thermodynamic stability as compared to VN under reaction conditions.[6] On burning off the excess carbon in air, VC and VN were found to be oxidised to vanadium oxide, which was readily soluble in 2% sodium hydroxide solution. No SiC or Si_2ON_2 were detected in the products. The SiC growth is not favoured in the presence of liquid V_2O_5 as in Fe–Si liquid[2,3,5] (iron catalyst) suggesting that V_2O_5 liquid is not able to take into solution a significant amount of carbon or carbon monoxide and silicon monoxide, through solid-liquid–vapour mechanism.

Figure 2(b) shows the morphology of the powder obtaining from nitridation of pyrolysed rice husk containing 2% V_2O_5. A marked difference is observed in the morphology of the powder obtained which consists of coilly fibrous particles

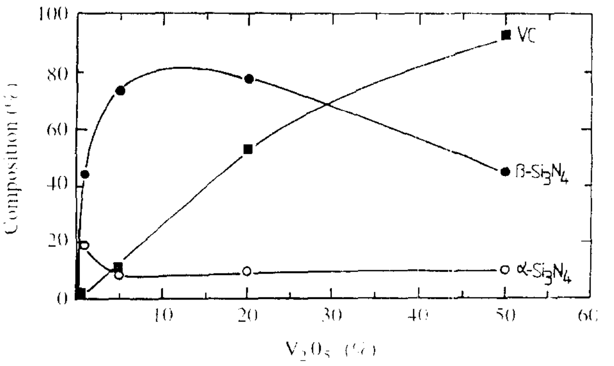
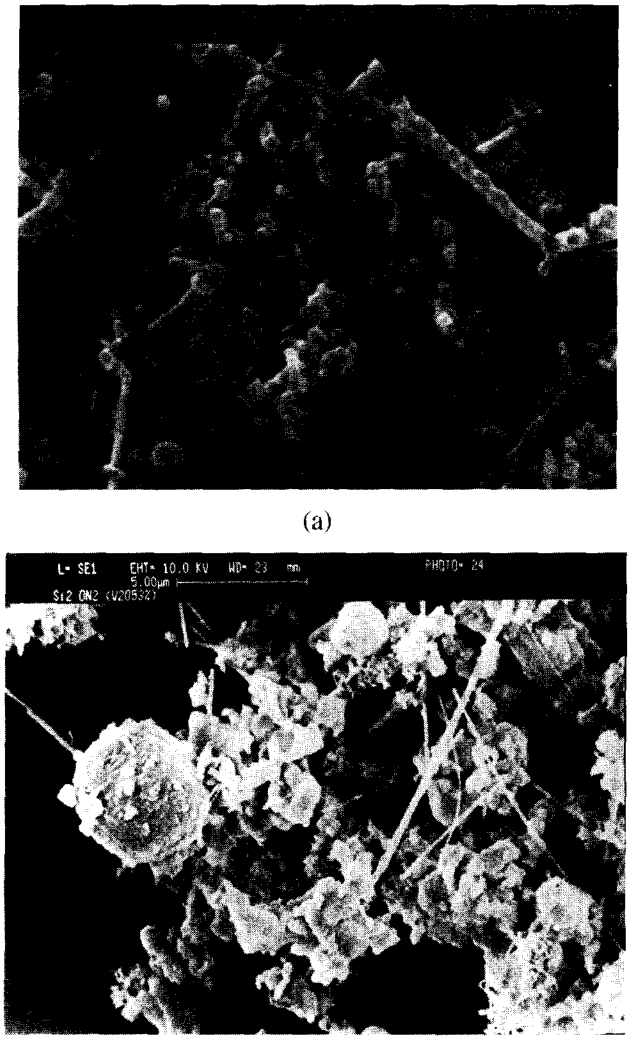


Fig. 3. The effect of V_2O_5 on nitridation of undigested rice husk.

of 1–2 µm. The nature of the powder morphology indicates that is grows in the present of liquid. This condition is not difficult to achieve since melting temperature of V_2O_5 is 690°C. This supports the observation that the products after nitridation has increased in volume like 'baked cake'.

Nitridation of digested rice husk

It was reported that an equiaxed, submicrometer and high α-phase silicon nitride powder was prepared by nitriding rice husk that previously digested with HNO_3.[7] The carbon and silica molar ratio in the starting husk was 2. The SEM of the powder is shown in Fig. 4(a).



(a)

(b)

Fig. 4. Scanning electron micrographs of Si_3N_4 powders obtained from nitridation of pyrolysed rice husk. (a) Digested husk; (b) digested husk + 3% V_2O_5.

Table 2. Phase composition of the powder prepared from nitridation of the digested rice husk incorporated with V_2O_5

V_2O_5(%)	Phase composition (%)		
	α-Si_3N_4	β-Si_3N_4	Si_2ON_2
0	92	8	—
3	11	9	80
7	10	11	79

The fact that V_2O_5 was found to be an effective catalyst for β-Si_3N_4 formation, led to further experiments using rice husk which was digested with HNO_3 as starting material. The husk was incorporated with V_2O_5 up to 7% and nitridation procedure was carried out in the same manner as for undigested husk. The product was found to consist mainly of Si_2ON_2 as shown in Fig. 4(b) and Table 2. VC and VN were also detected in the product. This phenomenon might be due to the carbon in the system being consumed by eqns (6) and (7). Thus, carbon to silica molar ratio is reduced below the stoichiometric ratio. This condition most likely caused the oxygen partial pressure to increase beyond 10^{-10} Pa. Therefore, the formation of Si_2ON_2 was favoured through eqn (8) and formed the predominant phase:

$$2SiO_2(g) + N_2(g) + 3C(s) = Si_2ON_2(s) + 3CO(g) \quad (8)$$

CONCLUSION

Si_3N_4 with a predominant β-Si_3N_4 phase could be obtained by carbothermal reduction of rice husk at 1430°C in the presence of V_2O_5 and in the condition of excess carbon. Si_2ON_2 appeared to be the predominant phase when carbon and silica content was reduced to the stoichiometric molar ratio of the overall carbothermal reduction reaction. This provides a comparatively cheap and easy way of producing β-Si_3N_4, α-Si_3N_4 and Si_2ON_2. However, α-Si_3N_4 could be obtained by nitridation of either undigested or digested rice husk without adding V_2O_5.

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REFERENCES

1. ZHANG, S. C. & CANNON, W. R., Preparation of silicon nitride from silica. *J. Am. Ceram. Soc.*, **67**(10) (1985) 691–695.
2. BONDYOPADHYAY, S. & MUKERJI, J., Reaction sequences in the synthesis of silicon nitride from quartz. *Ceram. Int.*, **17** (1991) 171–179.

3. EKELUND, M. & FORSLUND, B., Carbothermal preparation of silicon nitride: influence of starting material and synthesis parameters. *J. Am. Ceram. Soc.*, **75**(3) (1992) 532–539.
4. PERERA, D. S., Conversion of precipitated silica from geomethermal water to silicon nitride. *J. Mater. Sci.*, **22** (1987) 2411–2415.
5. SIDDIQI, S. A. & HENDRY, A., Influence of iron on the preparation of silicon nitride from silica. *J. Mater. Sci.*, **20** (1985) 3230–3238.
6. RAHMAN, I. & RILEY, F. L., The control of morphology in silicon nitride powder prepared from rice husk. *J. Eur. Ceram. Soc.*, **5** (1989) 11–22.
7. Rahman, I. A., Preparation of Si_3N_4 by carbothermal reduction of digested rice husk. *Ceram. Int.*, **20** (1994) 195–199.
8. LEE, J. G. & CUTLER, I. B., Reaction in the SiO_2–C–N_2systems. In *Nitrogen Ceramics*, ed. F. L. Riley. Noordhoff, Layden, 1977, pp 175–181.
9. TERWILLINGER, G. R. & LANGE, F. F., Hot-pressing behaviour of Si_3N_4. *J. Am. Ceram. Soc.*, **57**(1) (1974) 25–29.
10. LEE, D. D., KANG, S. J. L., PETZOW, G. & YOON, D. N., Effect of α to β(β') phase transition on the sintering of silicon nitride ceramics. *J. Am. Ceram. Soc.*, **73**(3) (1990) 767–769.
11. SAJGALIK, P., α/β phase transformation of Si_3N_4 without sintering additives. *J. Eur. Ceram. Soc.*, **8** (1991) 21–27.