



Synthesis of silicon nitride by conventional and microwave carbothermal reduction and nitridation of rice hulls



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ABSTRACT

Rice hulls were used as raw material to produce Si₃N₄ by conventional and microwave carbothermal reduction and nitridation. The precursor was made by the digestion of rice hulls with 12 M HNO₃, followed by pyrolysis of digested hulls to reduce the organic carbon. The precursor was then pelletized and reacted in conventional and microwave furnaces. The intimate of SiO₂ and carbon mixture favored the complete formation of Si₃N₄ in conventional reaction. However, SiC residual phase was present in the product of microwave reaction probably owing to the rapid temperature increasing of the reaction, caused by the thermal runaway effect of alumina pipe reactor.

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1. Introduction

Refractories are normally defined as materials which withstand high temperatures. For materials engineering, such materials are ceramics that are used as lining of high temperature processing furnaces at the industries of ceramics, metallurgical, glasses, etc. Silicon nitride is comprised as a special kind of refractories, whose properties qualify it to be applied in other areas, not only as refractory [1]. As a consequence of its unique mechanical performance, even in high temperatures it is also possible to use it as cutting tools or wear bearing parts [2]. In the early 1990s decade, researchers carried out investigations on the use of silicon nitride in microelectronics as thin films, nanowires and nanotubes [3]. Si₃N₄ was discovered at the end of 19th century and at that time it was not quite employed owing to its high production cost. In the 1950s new researches revealed the unique physical and chemical properties of Si₃N₄ and the interest in such material rapidly rose, which caused the development of novel processes to synthesize it. Since then, several researchers have worked to prepare and study its applications, as well as the effect of different polymorphic phases on the properties [4]. However, the high energy expense for production and processing the silicon nitride in industry has been the key factor to limit such interest. So, new routes for production of Si₃N₄ are desirable. A number of ceramic materials have been made and processed recently by use of microwave energy [5–12].

Microwaves permit to reaction kinetics to accelerate, mostly if an adequate microwave susceptor is assembled together with the reactants. The interactions between the microwaves and the materials result not only in fast heating, a marked decreasing in the activation energies of the reaction and an increase in diffusion rates of the process are strongly noted [5,6]. In the microwave carbothermal reduction and nitridation (MCTR), carbon acts as SiO₂ reducing agent and microwave susceptor, coupling with the electromagnetic energy to produce heating through Joule effect. So, an intimate blend of the reactants is essential to improve the reaction yielding. Deksnys et al. [12] in recent work synthesized Al₂O₃/SiC composite by microwave carbothermal reduction of a mixture of aluminosilicate and carbon black. They observed that SiC particles were formed in various morphologies, including whiskers and nanoparticles. Such researchers used a synthesis apparatus very similar to that which was developed in present work.

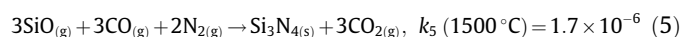
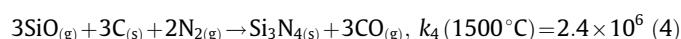
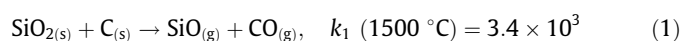
Carbothermal reduction has been commonly used to synthesize SiC [13–17], Si₃N₄ [18–21], TiC [22], AlN [23] and composites [11,24]. The solid state reactions occur in three steps: (i) transport of material through the interface; (ii) reactions at the vicinity of the interfaces; and (iii) Moving reaction products away from the interfaces. Along with solid state, vapor phase reactions frequently takes place during carbothermal and nitridation reactions, owing to SiO and CO gaseous products that are generated in high temperatures. Impurities, such as metallic oxides or carbonates act as catalyst sites to whisker growth by the VLS (vapor–liquid–solid) process [25]. Some vanadium compounds are effective in increase the Si₃N₄ production, but β-SiC was present as co-product at temperatures up to 1450 °C [21].

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Rice hulls have been used as silica source to prepare SiC [17], zeolite [26] and Si₃N₄ [11]. The SiO₂ in rice hulls comprises about 20% in weight, and other constituents are K₂O, CaO, MgO, MnO, Al₂O₃ and P₂O₅. The organic matter is composed of hemicellulose, cellulose (62.5%), and lignin (32.5%). Oil, proteins and other compounds are also present [27,28].

During Si₃N₄ formation in the CTR-N, some reactions are involved, as follow:



Reaction (1) is referred to SiO gas formation. Reactions (2) and (3) are gas–solid reduction reaction and reactions (4) and (5) are the nitridation of SiO in the vapor phase. An excess of carbon is required in the step of nitridation around 1500 °C in order to avoid the Si₂ON₂ intermediate phase. A C/SiO₂ molar ratio of 2 is enough to ensure that all carbon reacts with O₂ in the reaction atmosphere to form CO or CO₂ [4,21].

In this context, the aim of this work was to use microwaves as energy source to carry out carbothermal reduction and nitridation to synthesize Si₃N₄ starting from rice hulls, a low cost and abundant raw material. Besides the low energy consumption, this work also aimed to drastically reduce the reaction times of the Si₃N₄ synthesis.

2. Experimental

2.1. Materials

The rice hulls which were used in this work possessed 19% of inorganic matter and 95% of such was composed of SiO₂. The source of carbon to reduce the silica was originated from the organic matter of the hulls, which was digested and pyrolysed.

2.2. Rice hulls digestion

In order to increase the specific surface area of the SiO₂ in the rice hulls, a step of digestion was introduced. First, they were washed in distilled water and then digested in HNO₃ 12 M for 6 h at about 90 °C. After digestion, rice hulls were washed to eliminate any trace of acid and dried at 100 °C.

2.3. Pyrolysis

The digested rice hulls were milled into ball mill and the powder was pyrolysed at a tubular furnace (Lindberg) in argon atmosphere to reduce the organic carbon. The resulting powder was conformed into pellets and then reacted.

2.4. Carbothermal reduction and nitridation (CTR-N)

Conventional CTR-N was accomplished in a tubular furnace (Lindberg Blue/M) at 1500 °C for 2 h. A N₂ flow of 2 L/min was maintained to avoid oxidation of carbon and ensure the nitridation. Microwave CTRN was carried out in a semi-industrial microwave oven (Cober Electronics Inc.). A reaction system was developed to be inserted into the microwave oven. An alumina pipe, with one

Table 1
Microwave reactions setup.

	RS1		RS2		
Time (min)	10	25	10	20	10
Power (kW)	0.5	1.5	0.5	1.5	2.0
N ₂ Flow (L/min)	0.8	0.8	0.8	0.8	0.8

end opened and the other partially closed was used as reactor. The pellets were placed inside the pipe and a N₂ flow was inserted with a flow of 2 L/min. Two reactions setup were chosen to perform the reactions in microwave oven aiming to evaluate the best configuration of reactions, termed RS1 and RS2, described as follow (see Table 1):

3. Results and discussion

Table 2 shows the chemical composition of the rice hulls used as the raw material in this work. 95% of the inorganic portion of rice hulls is composed of silica, which was essential to achieve the results showed in this paper.

The digested rice hulls showed a yellowish color and a pasty shape, which was the evidence of breaking the carbon chains of cellulose. According to Rahman [15] the higher the digestion time, the lesser the carbon percent in the rice hulls. So, a digestion time of 6 h was established to the adequate carbon/silica ratio. After digestion of the hulls, a black color precursor was obtained indicating the presence of amorphous carbon, which is the ideal form to couple with microwaves. The precursor was composed of an intimate mixture of SiO₂ and carbon with a high specific surface area of 254 m² g⁻¹, which was indicative of a small particle powder.

A preliminary set of reactions were performed in a conventional furnace (CCTR) and the XRD result showed the presence of Si₃N₄ phase, as indicated in Fig. 1.

Ideal conditions were set for such reaction and the achievement of silicon nitride phase was feasible, with a temperature of 1500 °C, continuous N₂ flow and 2 h of soaking time. It was also observed that no intermediate SiC phase was formed after reaction. Fig. 2 depicts the SEM images of CCTR and Si₃N₄ particles with various shapes were formed such as hexagonal crystals and whiskers which were formed by the VLS process due to the presence of impurities in raw material (K₂O as major impurity) which acted as catalyst site.

Appropriate setups were chosen for microwave reactions (MCTR) in order to perform the reactions with low energy expend, but aiming only Si₃N₄ phase in the product. However, some problems were observed during reactions which avoided achieving the desired results. That is, the thermal runaway of the Al₂O₃ pipe reactor caused the break of the reactor, preventing the reaction to carry on. RS1 was a two-step reaction with 1.5 kW top power level. The resulting phases were SiC and α-Si₃N₄, according to XRD result of Fig. 3. Another time and power setup was chosen and called RS2, which was performed in three steps. The main difference between those two reaction modes was the presence of β-Si₃N₄ in the product (Fig. 4). SiC was present, but in smaller content than before. Such a result was the evidence of that reaction reached a temperature level over 1500 °C, higher than the temperature reaction of the CCTR.

The morphologies of the particles from MCTR (RS1 and RS2) were remarkably different from those of CCTR. Clusters of nanoparticles of β-Si₃N₄ were obtained as well as whiskers and hexagonal crystals of α-Si₃N₄. The presence of nanoscaled particles in the powder form MCTR was probably due to the smaller time of the reaction, about 40 min, in contrast to CCTR which took over 4 h to be complete. As smaller the reaction time, as the particles will not

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