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Synthesis of α-Si_3N_4 from Carbon Coated Silica by Carbothermal Reduction and Nitridation

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Abstract

The production of α-Si_3N_4 *powder was performed by carbothermal reduction and nitridation of carbon coated fumed silica precursor. The precursor is derived from a fumed silica and a hydrocarbon gas* (C_3H_6) *and provides intimate contact between the reactants. This yields a better distribution of carbon within the silica and inhibits the agglomeration among the oxides of silicon during the reactions, resulting in a more complete reaction and purer product at a comparatively low temperature. The* Si_3N_4 *powders produced at 1500°C for 5 h in flowing nitrogen gas have low oxygen content (1·2 wt%), submicrometer particles (0·3–0·7 μm), high α phase content and no agglomeration. © 1998 Published by Elsevier Science Limited. All rights reserved*

1 Introduction

Advanced structural ceramics have, in recent years, made significant inroads into applications that have been served traditionally by metals. Some of the areas where ceramics have been in use in significant proportions are biomaterials, because of their better compatibility with biological environs, wear parts and cutting tools, because of their high hardness and wear resistance compared to metals. Further applications where ceramics are expected to extensively replace metals are reciprocating engine components, heat exchangers and bearings. This is because modern engineering ceramics contain carefully controlled chemistry and deliberately designed microstructure to produce materials with unique combinations of properties that can enhance the performance of engineering systems.[1]

Silicon nitride is one of the most promising of the advanced ceramic materials. It is also the most extensively studied material for high temperature applications. This is because of its low density, high temperature strength, excellent thermal shock resistance and better reliability as compared to most ceramics. Some of the common applications of silicon nitride include cutting tools, bearings, reciprocating engine parts, wear and metal forming components and springs. Transportation related applications include automotive valves, turbocharger rotors and valve guides. Most notably, silicon nitride parts contribute to the reduction in emissions and increasing the efficiency in reciprocating engines and in enhancing the productivity in a variety of metal working processes. As a result, an estimated global market for silicon nitride is expected to reach $700 million by the turn of the century.[2]

While silicon nitride is a leading advanced ceramic material for high temperature structural applications, the quality of its mechanical properties is dependent upon several variables. Chief among these variables are density, microstructure (uniform grain size, fine grains), and the concentration of structural defects in a finished product. Silicon nitride powders used as starting material for product parts should have high surface area, high purity, uniform spherical particle morphology with fine grains, high alpha-silicon nitride content, and low oxygen and carbon content. When silicon nitride powders meet these criteria, product parts made therefrom possess outstanding mechanical, chemical and thermal properties for use in advanced components and composites fabrication.

The various currently available methods for the synthesis of silicon nitride powders are:

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1. Direct nitridation of silicon

$$3Si(s) + 2N_2(g) = Si_3N_4(s) \quad (1)$$

2. Silicon diimide process

$$SiCl_4(l) + 6NH_3(g) = Si(NH)_2(s) + 4NH_4Cl(s) \quad (2)$$

$$3Si(NH)_2(s) = Si_3N_4(s) + N_2(g) + 3H_2(g) \quad (3)$$

3. Vapor phase reaction process

$$3SiCl_4(g) + 4NH_3(g) = Si_3N_4(s) + 12HCl(g) \quad (4)$$

$$3SiH_4(g) + 4NH_3(g) = Si_3N_4(s) + 12H_2(g) \quad (5)$$

4. Carbothermal reduction

$$3SiO_2(s) + 2N2(g) + 6C(s) = Si_3N_4(s) + 6CO(g) \quad (6)$$

Each of the above processes has its merits and demerits. Process (1) uses readily available raw materials and is used to produce reaction bonded silicon nitride. However, the reaction is exothermic making it difficult to control and powder produced through this process is lumpy and has to be extensively milled before it can be used for advanced applications. Processes (2) and (3) produce very high quality silicon nitride powder with a high surface area and fine particle size, but they are prohibitively expensive. Process (4), the carbothermal reduction, is the cheapest process, but the silicon nitride produced has impurities, high oxygen content, low yield and is generally agglomerated to a high degree.[3]

It therefore is apparent that a need is present for a process that can produce high-quality silicon nitride powders for use in fabrication of advanced ceramic components and composites. Accordingly, the primary object of this paper is to provide a new process for synthesizing silicon nitride powders having high purity, high surface area, pressureless sinterability, and relatively low cost. The process described in this work avoids the expense of the first three methods while surmounting the inability of the fourth to produce a high quality end product. It maximizes the reaction rate between silica and carbon by improving the contact area between the reactants and by providing a better distribution of carbon within the silica.

1.1 Chemical reactions

The overall reaction for the carbothermal synthesis of silicon nitride is

$$3SiO_2(s) + 2N_2(g) + 6C(s) = Si_3N_4(s) + 6CO(g) K_7(1500°C) = 1{\cdot}001 \times 10^{-1} \quad (7)$$

The actual reaction, however, is generally agreed upon to go through several intermediate steps,[4] these being;

1. Generation of silicon monoxide phase:

$$SiO_2(s) + C(g) = SiO(g) + CO(g) K_8(1500°C) = 3{\cdot}619 \times 10^{-3} \quad (8)$$

$$SiO_2(s) + CO(g) = SiO(g) + CO_2(g) K_9(1500°C) = 3{\cdot}385 \times 10^{-7} \quad (9)$$

$$CO_2(g) + C(s) = 2CO(g) K_{10}(1500°C) = 1{\cdot}069 \times 10^4 \quad (10)$$

Thus the CO_2 produced in (9) and the C present, react to give CO and this further promotes reaction (9).

2. Formation of silicon nitride

$$3SiO(g) + 2N_2(g) + 3C(s) = Si_3N_4(s) + 3CO(g) K_{11}(1500°C) = 2{\cdot}112 \times 10^6 \quad (11)$$

$$3SiO(g) + 2N_2(g) + 3CO(g) = Si_3N_4(s) + 3CO_2(g) K_{12}(1500°C) = 1{\cdot}728 \times 10^{-6} \quad (12)$$

The overall reaction (7) has been reported to be slow. Increasing the reaction temperature, in order to improve the reaction rate cannot be used since SiC formation is favored at temperatures above 1500°C.[5] It has also been reported that the rate limiting step is the generation of SiO. Since this occurs by reactions (8) and (9), the rate can be improved by removing the byproduct CO.[6] This requires a higher gas flow rate of nitrogen. However, the gaseous silicon monoxide formed along with the carbon monoxide has a high vapor pressure and tends to be swept away and lost from the reaction chamber unless reacted with carbon. Also rate of reaction has been reported to be drastically increased by the addition of silicon nitride as seed.[7] The rate might further be improved by using more reactive (reducing) gases like NH_3 or N_2–H_2 mixture, but this results in the formation of HCN as a byproduct gas and hence is not practical.[8] Another way of improving the rate and the quality of the reaction products is to improve the quality of mixing of the reactants (silica and carbon) in carbothermal reduction nitridation process.

In the present work, the maximization of the reaction rate (the mixing quality of the reactants) was achieved by a new process; carbon coating of silica. Silica particles were coated with carbon by decomposing a hydrocarbon gas (C_3H_6) at a temperature of 600°C. This provides high surface contact between the reactants and an even distribution of carbon among the silica particles. The next step involves the formation of Si_3N_4 powders by promoting a carbothermal reduction and nitridation reaction within the carbon coated silica particles, in a nitrogen atmosphere at temperatures of 1100–1600°C.

2 Experimental Procedure

2.1 Starting materials

The starting silica powder was a very high surface area ($320\,m^2\,g^{-1}$) fumed silica from Cabot Corp. (Cabosil EH-5, Springfield, IL). The transmission electron microscopy (TEM) micrograph of the Cabosil EH-5 SiO_2 particles (Fig. 1) showed that it has an average particle size of 10 nm. These particles were in the form of three dimensional chain-like agglomerates, approximately 0·5–10 microns in size. Cabosil fumed silica is the purest commercially available amorphous silica. It contains at least 99·8% by weight silicon dioxide on an ignited weight basis. In several experiments, 10 wt% Si_3N_4 was added as a seed in the precursors to increase the reaction rate further. The seed used was α-Si_3N_4 (Hermann Starck, Grade M11-Leverkusen, Germany), with a BET surface area of $9{\cdot}6\,m^2\,g^{-1}$.

2.2 Preparation of carbon coated precursors

Silicon nitride powders were synthesized using the carbon coating process that was first reported by Glatzmaier and Koc.[9] A rotating coating reactor, consisting of a 10 cm ID×35 cm long stainless steel vessel, was used for producing carbon coated fumed silica particles. Propylene (C_3H_6) was used as the coating gas. About 80 g of fumed silica powder was placed in the vessel and the vessel was evacuated to a moderate vacuum level using a rotary vacuum pump. Then the vessel was filled with propylene gas until the pressure reached 2·7 atm. The vessel was then heated to 600°C. Thermal cracking of propylene increased the internal vessel pressure to about 3·5 atm upon initiation of the carbon coating. The coating step was continued until 36 wt% of carbon was deposited, which required about 28 cycles (each cycle was 5 min). The weight percentage of the carbon in the precursor was determined using thermogravimetric analysis in air.

Some of the precursors prepared were seeded up to 10 wt% with α-Si_3N_4. The carbon coated silica and $\alpha - Si_3N_4$ seed were placed in a plastic container (i.d. = 5 cm and height = 7 cm) and milled with two polymer balls for 20 min in a Spex (Model 8000 Mixer/mill, Meutuchen, NJ) mixer.

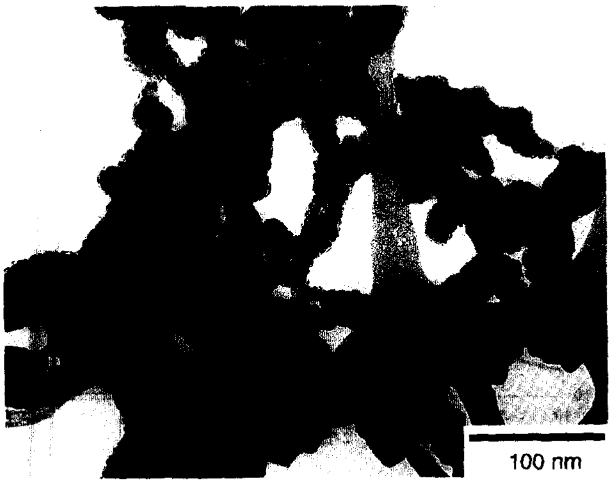

Fig. 1. TEM micrograph of starting fumed silica powder.

2.3 Synthesis of Si_3N_4 powders

The carbon coated silica precursors with and without seed were then synthesized in a tube furnace (Model CTF 17/75/300, Carbolite, Hope, Sheffield, UK) with an i.d. of 70 mm. Eight grams of a given sample for each temperature (1100, 1200, 1300, 1400, 1500 and 1600°C) were placed in a graphite crucible (i.d. = 65 mm and length = 10 cm). The furnace was first evacuated before a flowing stream of nitrogen at $1\,l\,min^{-1}$ was supplied. The Si_3N_4 powders were then produced by promoting a carbothermal reduction and nitridation between the carbon coated silica and nitrogen gas. The samples were synthesized at temperatures of 1100, 1200, 1300, 1400, 1500 and 1600°C for 5 h to investigate reaction mechanism and determine an optimal reaction temperature. A heating rate of $4°C\,min^{-1}$ and a cooling rate of $4°C\,min^{-1}$ was used.

2.4 Characterization of produced Si_3N_4 powders

The samples were subjected to XRD (Model DMAX-B, Rigaku, Tokyo, Japan) using CuK_α radiation for the study of phase evolution. Each sample was X-rayed in powder form at a scanning speed of $2°$–$2\theta\,min^{-1}$ and increment of 0·05 from 10 to 90°.

The surface areas of the powders were measured using a BET gas adsorption surface area analyzer (Micromeritics, Gemini 2360, Nocross, GA). Approximately 0·03 to 0·05 g of powder were placed in a test tube and allowed to degas for 4 h at 175°C in flowing nitrogen. This removes contaminants such as water vapor and adsorbed gases from the samples. After a sample was degassed, the surface area was analyzed and a BET multipoint surface area report was given based on the amounts of gases absorbed and the corresponding pressures.

Oxygen and nitrogen content of the produced powders were determined by Leco (St. Joseph, MI). The oxygen and nitrogen were analyzed by infrared detection in a Leco R0416DR induction furnace, while total carbon content was determined by burning the reaction products in air at 750°C for 4 h.

TEM (Model FA 7100, Hitachi Inc., Tokyo, Japan) studies were also performed. A small amount (0·5 g) of each sample was diluted in 25 ml of normal butanol slightly viscous alcohol and sonicated for 30 min. Three to four drops from an eye dropper of the sonicated samples were then placed on copper grids with holey carbon coated formvare. The samples were placed in a vacuum oven, to dry, before being examined.

3 Results and Discussion

Figure 2 shows TEM micrograph of the carbon coated fumed silica precursors. The darker areas are SiO_2 particles and the lighter areas surrounding the darker areas are the carbon coating. As shown in Fig. 2, an extremely uniform coating of pyrolytic carbon on SiO_2 is apparent. This coating of the silica particles can be confirmed by the BET surface area measurements of the precursors. The BET surface area of the SiO_2 ($320\,m^2\,g^{-1}$) decreases as carbon is coated on it, thus reducing it to the measured value of $160\,m^2\,g^{-1}$ for the carbon coated precursor. These results showed that uniform, highly porous and low density carbon coating can be obtained at 600°C on the SiO_2 particles by using C_3H_6 gas. The uniformity of the mixing by the present process is due to the carbon deposition on SiO_2 particles by cracking of hydrocarbon gas, although it was not possible to evaluate the uniformity quantitatively. These precursors are capable of producing high purity Si_3N_4 particles at low temperatures, because the carbon source is a hydrocarbon gas. Therefore, impurities, such as iron which is ordinarily found in commercial carbon material are eliminated. The use of carbon coated fumed silica precursor results in the production of submicron and uniform size Si_3N_4 particles, because the agglomeration of the oxides of silicon is also inhibited by a carbon layer.

Fig. 2. TEM micrograph of the carbon coated fume silica precursors.

Figures 3 and 4 are X-ray diffraction patterns of the reaction products of both the seeded and unseeded precursors, respectively. The X-ray diffraction results for the seeded precursor shows that the formation of silicon nitride is evident at 1400°C and is nearly complete at 1500°C. SiC formation can be clearly seen to occur at higher temperatures (T = 1600°C). The X-ray diffraction patterns of precursors without seed show almost no formation of silicon nitride at 1400°C. There is, however, significant formation of silicon nitride at 1500°C although comparatively much less than that for the seeded precursors. Thus the importance of using seed in carbon coated fumed silica precursors was also observed. The addition of Si_3N_4 powder as a seed to the carbon coated precursors significantly enhanced the nitriding reaction. This pattern can

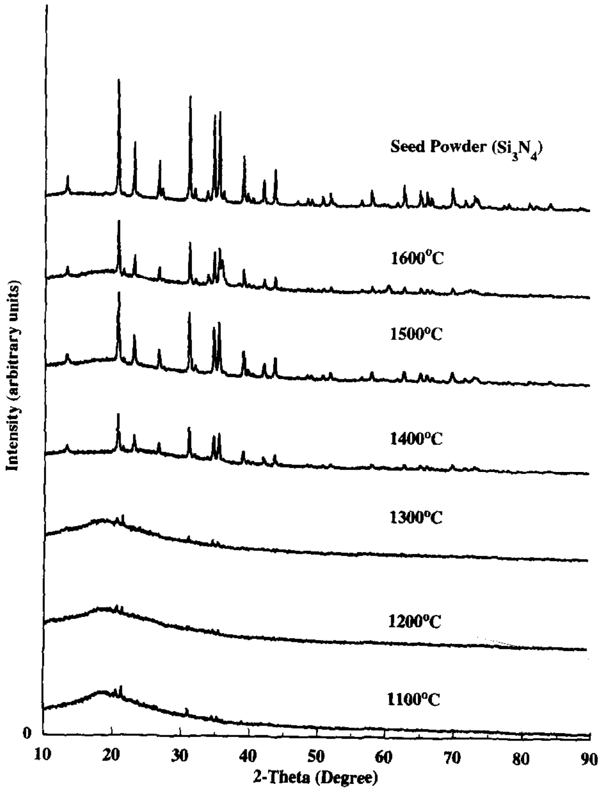

Fig. 3. XRD results of reaction products produced from seeded precursors at 1100–1600°C for 5 h in flowing nitrogen gas.

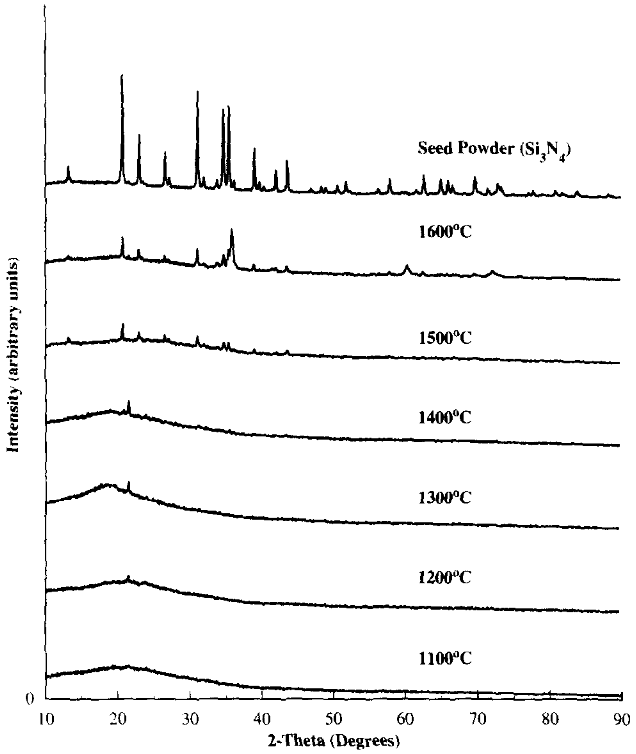

Fig. 4. XRD results of reaction products produced from unseeded precursors at 1100–1600°C for 5 h in flowing nitrogen gas.

also be seen in the weight loss measurements, which show an increase in the weight loss with an increase in the reaction temperature (Fig. 5). The X-ray diffraction patterns of the silicon nitride produced did not show any β-Si_3N_4. The seed powder used, however, contained some β-Si_3N_4. The traces of β-Si_3N_4 was observed from TEM investigation (Fig. 7).

The BET surface area measurements were made to obtain information about the reaction mechanism and the particle size of the product powders as a function of the reaction temperature. Before subjecting the samples to the BET surface area measurements, free carbon was removed by heat treatment at 750°C in air for 4 h. As can be seen from Fig. 6 the BET surface area of the reaction products from the seeded precursors, increased with reaction temperature to a maximum at 1200°C and then decreased as the reaction temperature increased. The increase in BET surface area may be related to the formation of silicon monoxide by solid-solid reactions. The decrease in the BET surface area from 1200 to 1600°C implies the completion of reaction towards the formation of silicon nitride.

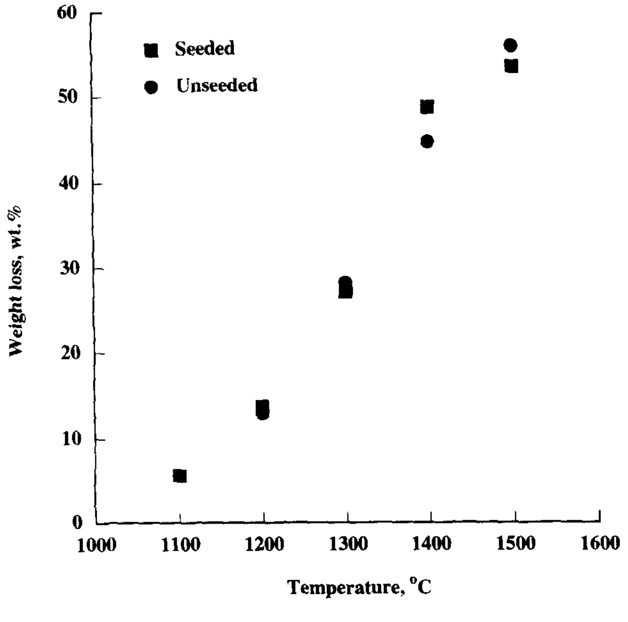

Fig. 5. Change in weight loss as a function of temperature for seeded and unseeded precursors.

TEM was used to investigate the particle size, size distribution, particle morphology and degree of agglomeration. Figure 7 shows a bright-field image of TEM micrograph of synthesized powders from seeded precursors at 1500°C for 5 h in 1 l min^{-1} flowing nitrogen gas. As can be seen from Fig. 7, the synthesized Si_3N_4 powders have a fine particle size, narrow particle size distribution and no agglomeration. The carbon coating process

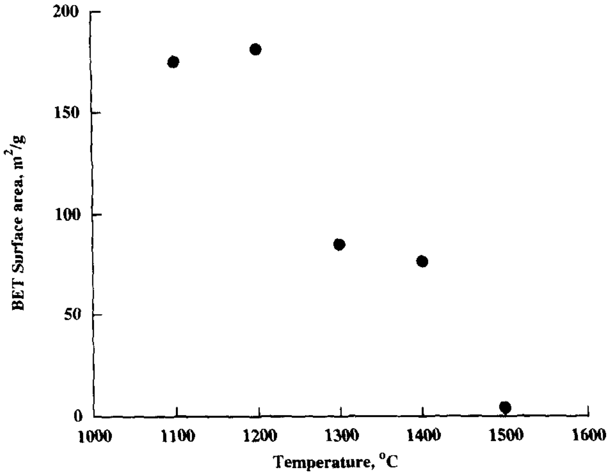

Fig. 6. Change in BET surface area as a function of temperature for seeded precursors,

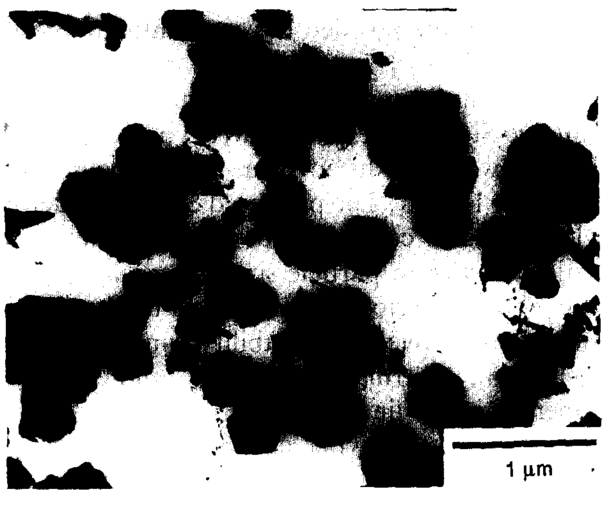

Fig. 7. TEM micrographs of produced powders from seeded precursors at 1500°C for 5 h in flowing nitrogen gas.

Table 1. Comparison of the produced Si_3N_4 powders from seeded precursors at 1500°C for 5 h in flowing nitrogen gas with commercially available powders

	Product powder	*H.C. Starck M11*
Particle size (µm)	0·3–0·7	0·5
BET surface area ($m^2 g^{-1}$)	4·5	9·6
Oxygen content (wt%)	1·2	1–2
Nitrogen content (wt%)	3·8	40

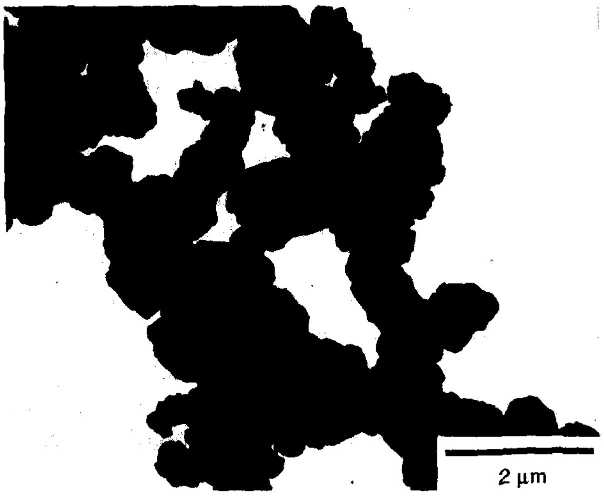

Fig. 8. TEM micrographs of produced powders from mixed precursors at 1500°C for 5 h in flowing nitrogen gas.

distributes carbon much more effectively and evenly across the entire volume of the precursor as can be observed from TEM micrographs of the precursor (Fig. 2). This ubiquitous presence of carbon tends to prevent the agglomeration of the Si_3N_4 particles formed during the reactions.

The chemical analysis of the product powders showed an almost identical nitrogen content for the silicon nitride from both the seeded and unseeded precursors at 1500°C. The oxygen content for both the powders was measured to be about 1·5 wt%. The free carbon content was determined to be 19 wt% for the powders produced from seeded precursors at 1500°C. After removing the free carbon from the powder, oxygen content increased from 1·2 wt% to 1·7 wt%. Table 1 provides a summary of the comparison between commercially available Si_3N_4 (H.C. Starck M11) powder and the Si_3N_4 powder produced from carbon coated precursors at 1500°C. The produced Si_3N_4 powder has a low oxygen content with submicrometer size particles, uniform particle size and no agglomeration. These superior characteristics of the powder lead to improved sinterability and to better mechanical, thermal, chemical, and electrical properties in the final products.

Fumed silica, 36 wt% carbon black (Monarch 880, Cabot, Waltham, MA) and 10 wt% Si_3N_4 seed powder were also dry mixed in a Spex mixer (Model 8000 Mixer/mill, Meutuchen, NJ) for 2 h in a plastic container and reacted at 1500°C for 5 h in flowing nitrogen gas for comparison. Figure 8 shows a TEM micrograph of synthesized Si_3N_4 powders from the mixed precursor at 1500°C for 5 h. The produced Si_3N_4 powders have large particle size (0·5–2·0 µm), oxygen content of 1·5 wt% and hard agglomerates.

4 Conclusion

The carbothermal reduction synthesis using carbon coated fumed SiO_2 precursor is capable of producing high quality silicon nitride suitable for advanced engineering applications. The powders were determined to be submicron, single α-phase and have high chemical purity and low oxygen content. Further, the Si_3N_4 powders produced from the carbon coated precursor were either superior, as determined from TEM studies, or equal, as determined from the chemical analysis and X-ray diffraction studies, to the ones produced from the conventional mixed precursor.

The economy of the coating process just in terms of the cost analysis can be appreciated when it is considered that during large scale production, coating of silica powders with carbon is much easier than the mechanical mixing of silica and carbon powders.

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