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Synthesis and characterization of silicon nitride powders produced in a d.c. thermal plasma reactor

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Ultra-fine silicon nitride powder was synthesized from the $SiCl_4$–NH_3–H_2–Ar system using a d.c. plasma torch reactor (production rate 150–400 g h^{-1}). The powder produced is pure white, fluffy and amorphous. The particles are spheroidal in shape with a mean diameter between 30–60 nm forming aggregates of 0.1–0.4 μm depending on the operational conditions. Chemical analysis on the crude powder handled at ambient atmosphere revealed: N(–NH_4Cl):37–39%, O:3–5% and Cl:2–3%. The amorphous powder can be crystallized around 1500 °C under nitrogen to give an α-phase content in excess of 90%. Infrared spectra can be used to semi-quantitatively determine the NH_4Cl content of the crude powder. That proportion is between 2.5 and 4%. The influence of some process parameters e.g. (N/Si and H_2/N molar ratios, internal pressure) on powder properties was also investigated. The N/Si molar ratio was found to be the most important parameter for the powder composition whereas the internal pressure plays a major role on the powder morphology.

1. Introduction

Silicon nitride is an interesting material for structural applications as it exhibits high strength at elevated temperature, high thermal shocks, creep and oxidation resistance in harsh environment. To obtain material with such properties, the starting powder characteristics, such as spherical in shape, a fine particle size with a narrow distribution, the absence of hard agglomerate and chemical purity, are essential.

Si_3N_4 can be produced using different synthetic paths and methods. The most common routes are: the use of silica via the carbothermic reduction [1–6], the direct nitridation of silicon [7–10] to form the so-called "reaction bonded silicon nitride" (RBSN), calcination of chosen polymers [11–13], the ammonolysis of silicon tetrachloride [14–18], and also the vapour phase reaction using the laser [19–21] or the plasma [22–26] as the heating source.

The production of silicon nitride using plasma as a thermal source is well established, at least at a laboratory scale. Various types of plasma DC, RF, and a combination of these two, called the hybrid plasma, were used with various starting materials. Chang *et al.* [22] have published a survey on different synthetic paths using the plasma reactor. These routes are the silicon and ammonia system, the silane and ammonia system, and the $SiCl_4$ and ammonia system.

The ammonia silicon tetrachloride system is often chosen. These reactants were injected in a hybrid plasma by several Japanese researchers [23–25]. The same system was also used with a plasma arc jet [26]. The silicon nitride powders obtained with these two methods are similar, with spherical particles, averaging between 10 and 40 nm in diameter, of amorphous silicon nitride. The Japanese groups have reported chemical compositions in the following range: Si 60 ± 2% wt and N 37 ± 0.5% wt. In the crude material, the NH_4Cl byproduct is present at a concentration between 2 and 3% and can be easily removed by a heat treatment under nitrogen at 400 °C.

Using the chemical system $SiCl_4$–NH_3–H_2–Ar and our own d.c. thermal plasma reactor, the aim of this work is to study the influence of some process parameters on the powder characteristics. The chosen process variables that will be looked at are the N/Si ($NH_3/SiCl_4$) and the H_2/N (H_2/NH_3) molar ratios, the argon carrier gas flow rate, and the internal pressure. The criterias for the evaluation of the influence of each parameter are the chemical composition and the powder morphology.

2. Experimental procedure

The apparatus used is described elsewhere [27], all reagents Ar, NH_3, H_2 and $SiCl_4$ (Aldrich Chem. Co., 99% pure) were used without further purification. The silicon tetrachloride was injected near the plasma gun and ammonia further downstream, in the tail flame of the plasma torch.

For parameters optimization, all the experiments were performed with an argon plasma with a fixed current of 400 A, for a plasma power depending on the operating conditions and especially the pressure, between 10 and 11 kW. The optimization study is

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based on 4 min runs with a $SiCl_4$ feeding rate of 11.0 g min^{-1}. The powders were retained on a metallic filter of known porosity (10 μm pores). The powders were collected and handled at ambient atmosphere.

Infrared spectra were recorded on a Bomem Michelson 100 Fourier transform infrared spectrometer with samples prepared as KBr discs. X-ray diffraction patterns were recorded on a Phillips PW 1840 diffractometer using the Cu radiation (wavelength: 15.425 nm). Total nitrogen and oxygen content were determined on a LECO nitrogen oxygen analyser. Chlorine content was performed by ionic chromatography. The sample was prepared as follows: 0.05 g of Si_3N_4 was dispersed in 5 ml of methanol in an ultrasonic bath and completed to 100 ml with water and stirred. The resulting suspension was filtered with a 0.22 μm filter and injected by 50 μl portions in the column. Electronic microscopy was performed on a JEOL JSM 6100. Particle size analysis was performed on a B.I.C. 90 instrument, using methanol as the suspending media.

3. Results and discussion

3.1. Optimization of the process parameters

Initially four process parameters, namely N/Si ($NH_3/SiCl_4$) and H_2/N (H_2/NH_3) molar ratios, as well as the internal pressure and the argon carrier gas flow rate for silicon tetrachloride injection, were investigated to determine their effect on the powder properties. In the literature [23–26], silicon nitride powders were successfully produced with a wide variety of N/Si molar ratios and in most cases, an excess of ammonia was used. With our reactor, there is no need to use a larger N/Si molar ratio value than the natural stoichiometry 1.33. In fact, running with a higher than stoichiometric ratio, induces the formation of ammonium chloride at the expense of Si_3N_4, as presented in Fig. 1.

Unlike the production of silicon carbide, where the H_2/C molar ratio is critical to the powder production [27], the H_2/N molar ratio does not seem to exert the same type of effect on the silicon nitride powder production, as shown in Fig. 2. For H_2/N molar ratio values between 3 and 10, the effect seems to be negligible but as soon as the H_2/N molar ratio value is raised above 10, the formation of ammonium chloride increases drastically, detrimental to the Si_3N_4 formation. This situation tends to demonstrate that at higher H_2/N molar ratio values, the temperature in the reaction zone is no longer suitable for the formation of silicon nitride as the temperature is too low.

The influence of the Ar carrier gas flow rate is not very noticeable between 3 and 8 l min^{-1}, as shown in Fig. 3. However, with a value below 3 l min^{-1}, the powder composition is slightly affected by a diminution of the nitrogen content.

As presented in Fig. 4 the effect of the internal pressure on the powder composition is not evident. In

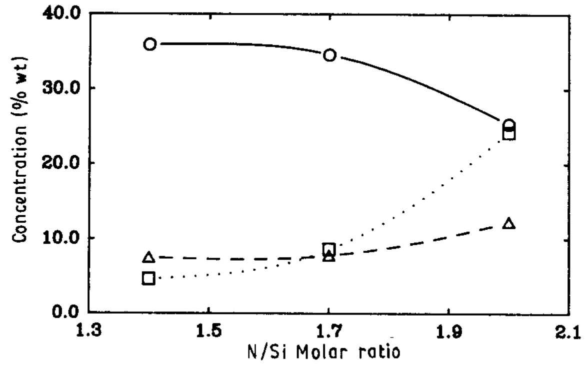

Figure 1 Composition variation as a function of the N/Si molar ratio for $H_2/N = 10$, Ar carrier gas flow rate = 3 l min^{-1} and internal pressure = 35 kPa. ○–○ is N(–NH_4Cl); △–△ is O and □ . . . . □ is NH_4Cl.

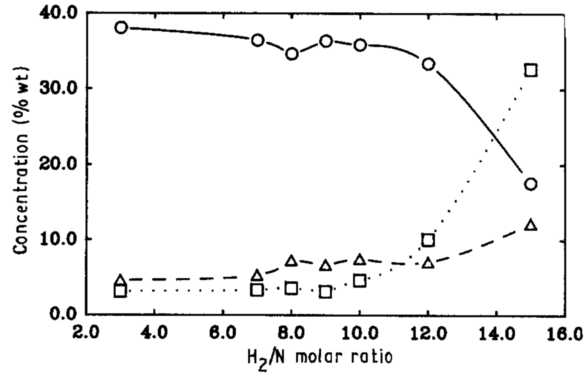

Figure 2 Composition variation as a function of the H_2/N molar ratio for N/Si = 1.4, Ar carrier gas flow rate = 3 l min^{-1}, and internal pressure = 35 kPa. ○–○ is N(–NH_4Cl); △–△ is O and □ . . . . □ is NH_4Cl.

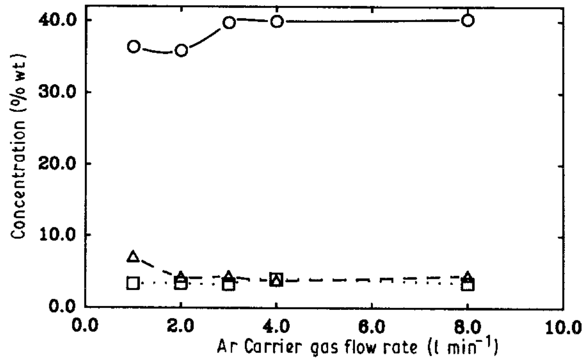

Figure 3 Composition variation as a function of the Ar carrier gas flow rate for N/Si = 1.33, $H_2/N = 8$ and internal pressure = 35 kPa. ○–○ is N(–NH_4Cl); △–△ is O and □ . . . □ is NH_4Cl.

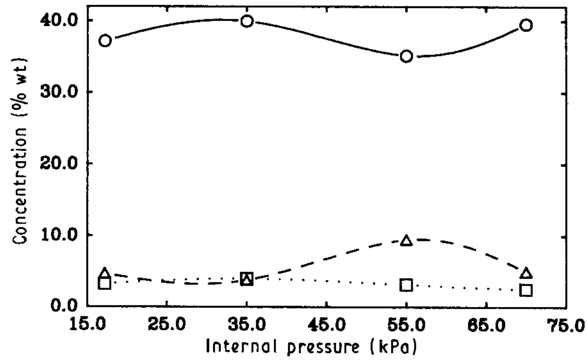

Figure 4 Composition variation as a function of the internal pressure for N/Si = 1.33, $H_2/N = 8$ and Ar carrier gas flow rate = 3 l min^{-1}. ○–○ is N(–NH_4Cl); △–△ is O and □ . . . . □ is NH_4Cl.

fact, the powder composition seems to deviate randomly around a mean average value, with no distinct relation to the internal pressure. However, the internal pressure seems to have an influence on the powder morphology, as demonstrated by particle size analysis.

At lower pressure value (17 kPa), the mean diameter of the particles is smaller (around 0.2 μm) than the one found at higher internal pressure value (70 kPa, 0.2–0.4 μm). These measurements are not related to the size of individual particles (or grains), but rather to aggregates of individual particles, as presented in Fig. 5 by SEM micrographs. On these micrographs, we can see spheroidal grains of 30 to 60 nm in diameter which form aggregates. At lower internal pressure value (Fig. 5a), the aggregates are smaller and more uniform in size than the one produced with a higher internal pressure value (Fig. 5b). It is not possible to detect if the internal pressure does have an effect on the size of grains. The aggregates are probably partially sintered, since attempts to break those aggregates with ultrasonic treatments up to 1.5 hours are not sufficient.

The effect of the internal pressure probably results from the following phenomenon: a pressure increase tends to confine the plasma, producing higher voltage and reaction zone modifications. From these observations, we can say that for powder reproducibility, the internal pressure must be controlled and constant during a production run.

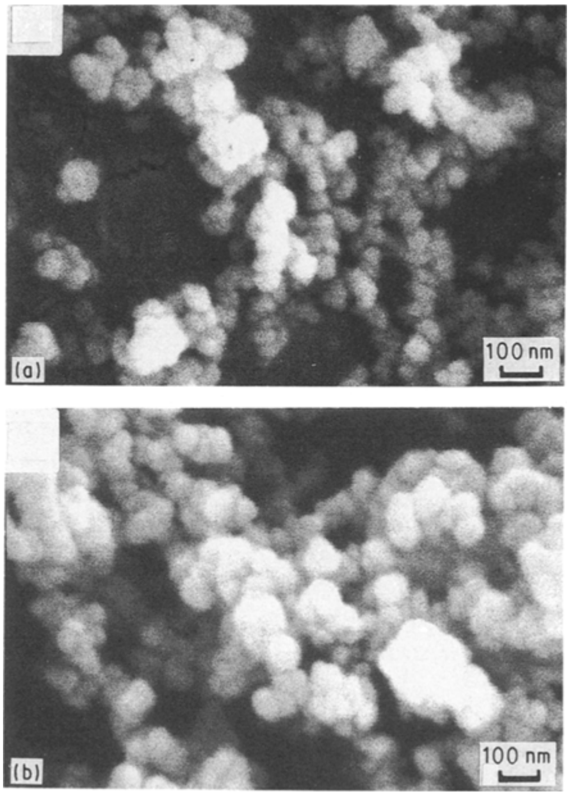

Figure 5 SEM micrographs of the as-produced silicon nitride powders for N/Si = 1.33, H_2/N = 8, Ar carrier gas flow rate = 4 l min^{-1} and internal pressure of (a) 17 kPa and (b) 70 kPa.

3.2. Physical characterization

Fig. 6 presents the infrared spectra of a Si_3N_4 sample before and after the heat treatment under nitrogen at 1530 °C. As you can see from that figure, the crude powder presents the typical spectrum for an amorphous Si_3N_4 powder, with no splitting or fine structure in the major peak around 995 cm^{-1} [28], related to the Si–N vibrations. After the heat treatment, the infrared absorption related to the NH_4Cl byproduct around 3150 and 1402 cm^{-1} are washed out, since sublimation of ammonium chloride occurs below 600 °C. The traces of water present (bands at 1625 and 3440 cm^{-1}) in the as-produced powder are believed to be related to hydrated potassium bromide.

The absorption spectra can also be used to evaluate in a coarse manner, the concentration of ammonium chloride in the as-produced powder, from the maximum absorption value registered for the ammonium chloride band at 1402 cm^{-1} and for the Si–N vibrations around 990 cm^{-1}. There is a linear relationship between the ratio R of the absorption value of the band at 1402 cm^{-1} over the absorption of the Si–N band at 990 cm^{-1} and the ammonium chloride weight percentage concentration. The relation can be evaluated from the plot in Fig. 7

$$NH_4Cl(\%\,wt) = 39.2R + 1.6$$

$$R = (\mathrm{abs\,NH_4Cl_{(1402)}/abs\,Si\text{–}N_{(990)}})$$

Although not designed to be an analytical method, the ammonium chloride concentration values obtained with that relation are, in most cases, the actual value more or less, 1% of NH_4Cl.

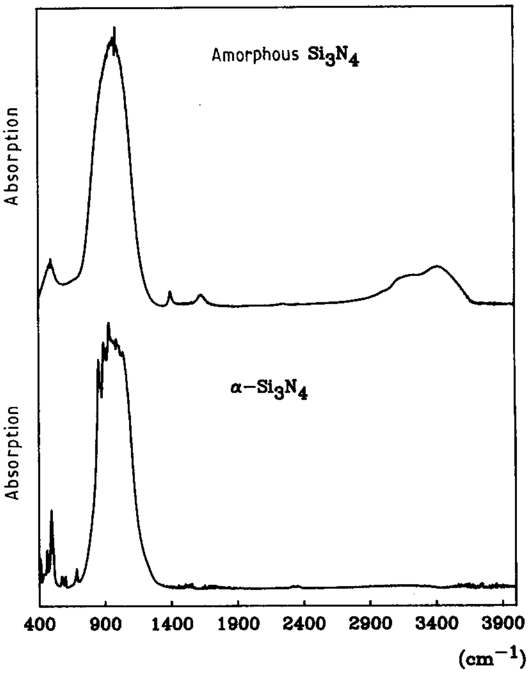

Figure 6 Infrared spectra for the as-produced amorphous Si_3N_4 powder and for the α-silicon nitride resulting from the heat treatment.

The X-ray diffraction pattern of the as-produced powder, Fig. 8a, also confirms the amorphous phase of the powder. The peaks present at the 2θ angle of 23.00, 32.74 and 58.08° are related to the presence of ammonium chloride. The other very weak bands that emerge

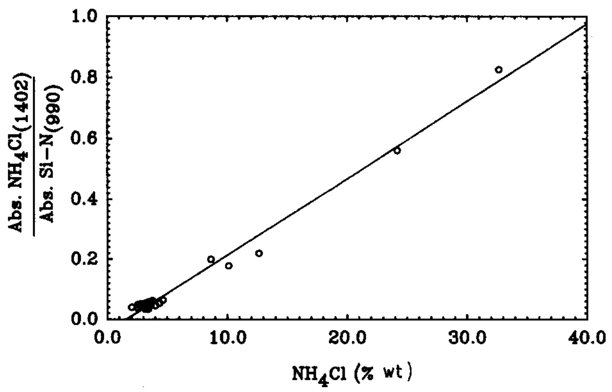

Figure 7 Variation of R as a function on the NH_4Cl content in Si_3N_4.

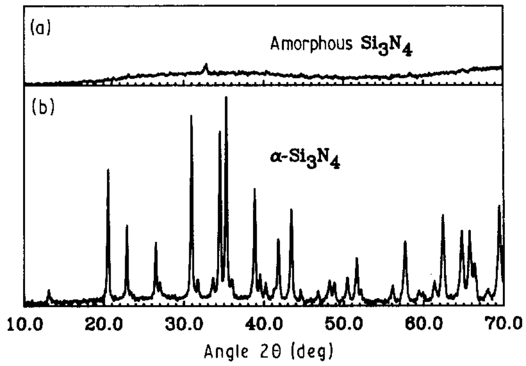

Figure 8 X-ray diffraction patterns of (a) the as-produced powder, and (b) the crystallized powder.

from the baseline, are associated to the α-phase of silicon nitride. The appearance of these bands and those of ammonium chloride, are closely related to the process parameters used in the production of the silicon nitride under investigation. However, in all cases the proportion of crystalline silicon nitride is very weak. As seen from the infrared spectra, the heat treatment eliminates the presence of ammonium chloride, which is confirmed by the X-ray diffraction pattern of the heat treated powder.

Amorphous silicon nitride can be crystallized by a heat treatment under nitrogen at around 1500 °C, to produce mainly α-silicon nitride and some β-silicon nitride. The X-ray diffraction pattern of the crystalline powder is presented in Fig. 8b. From that pattern, the proportion of the α-phase is not less than 90%, an estimation based on the formula presented by Mencik *et al.* [29]. The α-phase of silicon nitride also exhibits a characteristic infrared absorption spectrum as shown in Fig. 6. In fact, the crystallization process can easily be followed by both methods and the α/β-phase proportions can also be derived from the infrared spectra [30].

3.3. Production rate

Although the experiment on the influence of selected process parameters was performed at a fixed silicon tetrachloride feeding rate of 11.0 g min^{-1}, this is by no means a limitation imposed by the plasma reactor. In fact, using the same plasma power of 10.5 kW, silicon nitride was successfully produced with a $SiCl_4$ feeding rate up to 30 g min^{-1}. The N/Si molar ratio was kept at 1.33, while the H_2/N molar ratio had to be lowered as the $SiCl_4$ feeding rate was raised, to keep an efficient reaction zone. Silicon nitride was collected at a rate up to 400 g h^{-1}.

4. Conclusion

Silicon nitride was produced at a rate up to 400 g h^{-1}. The as-produced powder of the following composition: N(−NH_4Cl):37–39%, Si:53–56%, O:3–5%, NH_4Cl:2.5–4.0%, is pure white and amorphous. Spheroidal particles averaging between 30 and 60 nm in size, form agglomerates of 0.1 to 0.4 μm depending on the reactor's internal pressure. The ammonium chloride byproduct can be easily removed while the oxygen content can be drastically lowered by handling the powder under dry nitrogen. Crystallization of the amorphous powder occurs around 1500 °C, to produce mainly α-Si_3N_4. The most important process parameter is the N/Si molar ratio (1.33 for our reactor); the H_2/N molar ratio must be lowered as the silicon chloride feeding rate increases and the internal pressure affects the aggregation state of the powder.

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