SYNTHESIS OF Si_3N_4 POWDER BY THERMAL DECOMPOSITION OF $SI(NH)_2$

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ABSTRACT

A fine white α-Si_3N_4 powder has been produced by the thermal decomposition of the coprecipitation product of the reaction between $SiCl_4$ and NH_3. The Cl content, due to a reaction between $Si(NH)_2$ and the NH_4Cl by-product during the thermal treatment of the coprecipitate, has been reduced by using an isothermal step at ≈ 250°C in the heat treatment cycle.

INTRODUCTION

Although silicon nitride had already been isolated in 1844[1], it was not until 1960 that it was introduced as an engineering material by Parr et al[2]. Its outstanding combination of properties[3] -high strength, wear resistance, high decomposition temperature, creep and oxidation resistance in hostile atmospheres, good thermal shock resistance and low coefficient of friction- make it an ideal material for high temperature heat engine applications. The optimal performance and reliability of an advanced ceramic material is also determined by the densification process and the properties of the raw powder.

Several silicon nitride powder characteristics have been defined[4] for a good sinterability: Fineness to promote sintering[5], spherical shape for a good green compaction behavior, narrow size distribution[6] to inhibit grain growth. Chemical purity is also of major importance as an excessive impurity content can affect the final properties and the densification behavior. Rhodes et al[7] describe different types of impurities: Discrete inorganic or organic particles such as Fe. Anion impurities and organic compounds, that are often found in powders even after heating. In the case of silicon nitride, oxygen is the most common impurity, it forms films of SiO_2 or Si_2ON_2 on the surface of particles which may react with sintering aids such as Y_2O_3 to promote sintering, but an excess of oxygen can affect the elevated temperature strength and creep resistance, by changing the secondary phase composition. Another anion impurity is Cl which appears to inhibit the α to β transformation during sintering[8] and affect the final properties of the silicon nitride. Cation impurities, which usually concentrate as a second phase because of their poor solubility in the major phase, an example is the concentration of Ca[9] in the grain-boundary phase employed as a sintering aid for silicon nitride, this cation lowers the viscosity of the secondary phase and consequently the creep properties of silicon nitride.

Powder properties and also production cost[10] are determined by the silicon nitride powder synthesis route. Industrial processes for the production of silicon nitride powders are:

a) Direct nitridation of silicon powder with nitrogen gas at elevated temperatures.

b) Carbothermal reduction of silica powder with nitrogen in presence of carbon at high temperatures.

c) Reactions between silicon halide, such as silicon tetrachloride and silane[11], and ammonia either in gas-phase (commercially available[6] since the 1970s) or in liquid-phase[12,13] sometimes followed by a thermal decomposition step.

Thermal decomposition of the reaction-product between silicon tetrachloride and ammonia is one of the more promising methods for producing high quality silicon nitride powder. The purity of the powder, other than C and Cl impurities, is controlled by reactant purity, commercially available in a highly pure state. Powder morphology and size distribution may be controlled by monitoring reactant supersaturation. Costs are low as little or no powder grinding/cleaning processes are needed, and the possibility of conducting the reaction at room temperature and as a continuous process make it more attractive.

The aim of the current work was to study the precipitation-thermal decomposition route with respect to powder quality. Particular emphasis has been placed on the thermal decomposition of the $Si(NH)_2$ / NH_4Cl coprecipitate and our results are compared with various mechanisms proposed in the literature.

EXPERIMENTAL

Silicon nitride powder was produced in a two-step process: first the precipitation reaction (1) of liquid silicon tetrachloride with gaseous ammonia at 0°C in hexane was conducted in a batch reactor, followed by the thermal decomposition of the products to obtain silicon nitride.

Precipitation

In a glove box under a nitrogen atmosphere, containing < 3 ppm O_2 and < 5 ppm H_2O, silicon tetrachloride (puriss. Fluka), without further purification, was introduced into a reactor containing hexane (pro analysi Merck), dried with molecular sieve. Ammonia (electronic-grade Carbagas) diluted with nitrogen (>99.995% Carbagas) was bubbled into the silicon tetrachloride solution, with continuous stirring at 0°C (using a water-ice bath), fig.1. The use of nitrogen has two purposes, to avoid moisture and oxygen contamination and to control the ammonia concentration in the gas flow.

Hexane was evaporated under a low vacuum with a small flux of nitrogen, at 45°C in a rotatory evaporator. Powders where handled and stored in a glove box. Typical reactant concentrations are: 7.6×10^{-2} M $SiCl_4$, 4×10^{-3} mol/min NH_3.

$$SiCl_4\ (l) + 6\,NH_3\ (g) \xrightarrow{\text{hexane/0°C}} Si(NH)_2\ (s) + 4\,NH_4Cl\ (s) \qquad (1)$$

Thermal Decomposition

The coprecipitate $Si(NH)_2$ and NH_4Cl is then heat treated in a long tube furnace, after purging with nitrogen, at temperatures around 1400°C for ≈4 hours under flowing nitrogen, to produce sub-micron α-phase silicon nitride powder.

Analysis

The thermal decomposition of the coprecipitate $Si(NH)_2$ and NH_4Cl has been studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (TA4000 Mettler system). All powder manipulations were carried out under a nitrogen atmosphere. Concurrent studies were made on $Si(NH)_2$ after removing the NH_4Cl by-product by washing the coprecipitate with liquid ammonia at -68°C. Diffuse reflectance measurements (Nicolet 700 FTIR), XRD (Siemens D500 difractometer, Kα ray of Cu), particle size distributions (Horiba Capa700), elemental analysis (Perkin Elmer 2400CHN Elemental Analyzer), Si content (gravimetry), and Cl content (titration with silver nitrate in the presence of potassium chromate) analyses were used to characterize the various powder samples.

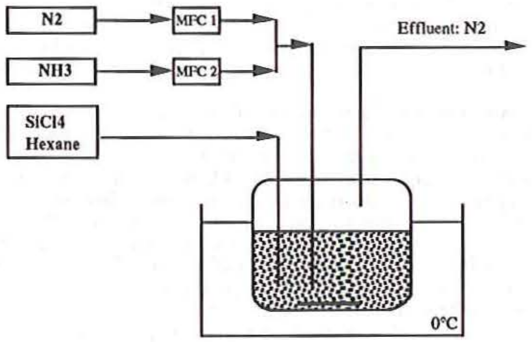

Fig.1 Schematic representation of the precipitation batch-reactor, for the reaction between $SiCl_4$ and NH_3. MFC 1 and MFC 2 are gas mass flow controllers.

Table I. Elemental analysis of different samples and theoretical compositions.
(+ a single data point , * two step heat treatment) (analysis precision ± 5%).

Sample	Formula	Si [wt%]	N [wt%]	H [wt%]	C [wt%]	Cl [wt%]	Si/N	N/H
theoretical	$Si(NH)_2$ + $4NH_4Cl$	10.3	30.9	6.7	-	52.1	0.3	4.6
coprecip.	$Si(NH)_2$ + $4NH_4Cl$	8.6	32.0	6.2	0.4	53.2	0.27	5.2
theoretical	$Si(NH)_2$	48.3	48.2	3.5	-	-	1.0	13.8
washed coprecip.		33.3	36.1	5.3	1.6	7+	0.9	6.8
LC StarcK	Si_3N_4	60.1	39.9	-	0.2	-	1.5	
sample	Si_3N_4	not det..	39.5	0	0.18	1.8 < 0.01*		

RESULTS AND DISCUSSION

Precipitation

With the addition of ammonia to the silicon tetrachloride solution, precipitation takes place immediately, and a white slurry of silicon diimide and ammonium tetrachloride is formed in hexane. The reaction yield is ≈100% and a typical product concentration is 4.4 g/l of $Si(NH)_2$.

The dried precipitation products are fine white powders, readily charged electrostatically and therefore difficult to manipulate, they hydrolyze on contact with moisture decomposing to SiO_2 and evolving ammonia.

Elemental analyses of the coprecipitate, table I, show a molar ratio close to 1/4 for $Si(NH)_2/NH_4Cl$ (calculated from the Si/N weight ratio).

The infrared spectrum of the coprecipitate, Fig.2 a, shows characteristic bands of NH_4Cl: 3140, 3040, 2825 cm^{-1} (NH asymmetric elongation), 2010, 1760 cm^{-1} (NH vibration broad bands), 1400 cm^{-1} (NH bending vibration), and 1060 cm^{-1}. In the spectra of $Si(NH)_2$, washed coprecipitate, Fig.2 b, these peaks practically disappear, except the one at 1060 cm^{-1}, which also corresponds to SiN vibrations. The bands centered at 3335, 1545 and 1210[14] cm^{-1} (NH_2 stretching vibration and scissors bending vibration[15]) are more visible in trace b. SiN and Si characteristic bands are present in both traces: 970, 830 cm^{-1} (SiN stretching vibrations) and 430 cm^{-1} (Si breathing vibration). Vibration bands associated with SiH (2100, 2200 cm^{-1}) are not present in either trace. Absorption associated with SiO vibrations occur at 800 and 1100, because of the overlapping of these bands with SiN bands, the existance of SiO_2 cannot easily be determined by this method.

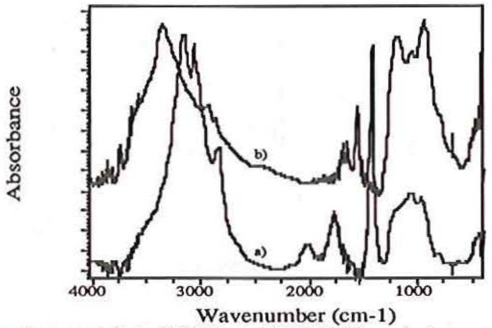

Fig.2 FTIR data: a) coprecipitate $Si(NH)_2 + 4\ NH_4Cl$, b) washed coprecipitate.

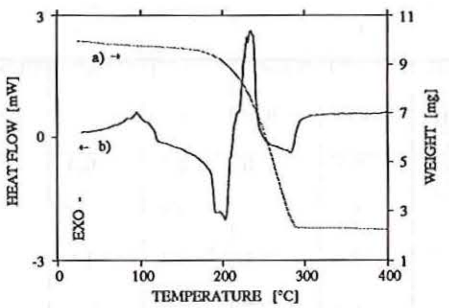

Fig.3 Thermal analysis of the coprecipitate ($Si(NH)_2$ + 4 NH_4Cl): a) TGA, b) DSC.

Thermal Decomposition

During the thermal decomposition of the coprecipitate $Si(NH)_2$ + 4 NH_4Cl a large weight loss (≈78%) takes place between 200-300°C, Fig.3 a, which mostly corresponds to NH_4Cl dissociation/evaporation. A smooth weight loss is also observed beginning almost at room temperature to ≈200°C and between 300-≈700°C attributed to the decomposition of $Si(NH)_2$ with the evolution of NH_3.

In the same fig. 3, the corresponding DSC data shows at first an exothermic peak around 100°C attributed to the decomposition of $Si(NH)_2$. Then in contradiction to the strongly endothermic peak expected for the sublimation of NH_4Cl around 300°C (see the DSC trace for NH_4Cl in the inset in Fig.4), a complicated trace appears between 200-300°C. The exothermic peak visible at ≈ 250°C could be due to further decomposition of an intermediate Si compound, or to a reaction between an intermediate Si compound and NH_4Cl. The thermal decomposition of NH_4Cl-free $Si(NH)_2$ (washed coprecipitate) shows no exothermic peak in this region, Fig.4 a), therefore a reaction between an Si compound and NH_4Cl around 250°C is proposed.

The thermal decomposition of a partially washed coprecipitate, Fig.4 b, shows the same trend as the coprecipitate in that an exothermic peak between 200-300°C is present, and because the amount of NH_4Cl available for sublimation is much less the heat effect at ≈250 °C

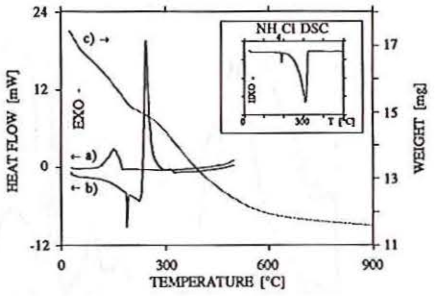

Fig.4 DSC data: a) washed coprecipitate ($Si(NH)_2$), b) partially washed coprecipitate ($Si(NH)_2$ + x NH_4Cl), c) TGA of partially washed coprecipitate ($Si(NH)_2$ + y NH_4Cl). NH_4Cl DSC included in the inset.

is more marked in this case, thus the hypothesis of a superposition of two phenomena taking place between 200-300°C (sublimation of NH_4Cl and reaction of a Si compound and NH_4Cl) is supported.

Several decomposition mechanisms have been proposed in the literature for the thermal decomposition of the $Si(NH)_2/NH_4Cl$ coprecipitate into Si_3N_4. Based on thermogravimetric data some authors[13, 16 and 17] proposed a decomposition-mechanism for the Si compound assuming a complete sublimation of NH_4Cl taking place simultaneously with the $Si(NH)_2$ decomposition. Billy[18] followed by others[19] proposed a mechanism which is consistent with much of our data:

$$Si(NH)_2 \xrightarrow{60°\text{-}80°C} 1/2\ Si_2N_3H + 1/2\ NH_3 \quad (2)$$

$$1/2\ Si_2N_3H + 1/2\ NH_4Cl \xrightarrow{130°\text{-}150°C} 1/2\ Si_2N_3H_2Cl + 1/2\ NH_3 \quad (3)$$

$$1/2\ Si_2N_3H_2Cl \xrightarrow{300°\text{-}400°C} 1/3\ Si_3N_4HCl + 1/6\ NH_4Cl \quad (4)$$

$$1/3\ Si_3N_4HCl \xrightarrow{> 400°C} 1/3\ Si_3N_4\ \text{(amorphous)} + 1/6\ HCl \quad (5)$$

Interpretation of our TGA/DSC data, Fig.3 and 4, is as follows. Reaction (2) takes place at 40-200°C, it is catalyzed by NH_4Cl, this reaction seems to take place at 80-200°C in absence of NH_4Cl. Between 200-350°C the reaction (3) between the Si compound and NH_4Cl is completed. Each of these steps incorporates the loss of 1/2 mole of NH_3 (10wt%). Further decomposition takes place with no apparent heat effect. The weight change observed between ≈40-200°C is ≈10 wt% (as expected for reaction (2)). In Fig.4 c (a partially washed coprecipitate) a continuous weight loss is observed from 200°C to > 700°C, the total amount of this weight loss is about 27.5 wt% which corresponds to the evolution of 1/2 mol NH_3 (10wt%) during reaction (3), 1/6 mol NH_4Cl (10.5 wt%) by reaction (4) and 1/6 mol HCl (7.2 wt%) by reaction (5). A steep weight loss is observed from room temperature to ≈40°C which might be due to the evolution of NH_3 adsorbed on the surface of the particles, or to an initial Si compound such as $Si(NH_2)_4$[19] which transforms into $Si(NH)_2$, FTIR shows evidence for the existence of NH_2 vibration modes, but they could also come from the $Si(NH)_2$ molecule with the structural formula: $N{=}Si{-}NH_2$.

Billy's work was carried out in vacuum, this could explain the differences in reaction temperatures when compared with our data.

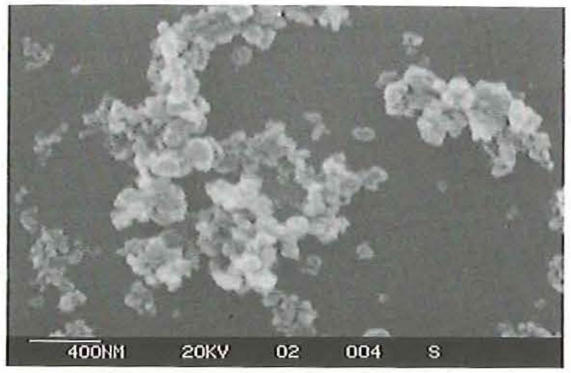

Fig.5 α-Silicon Nitride SEM image

Silicon Nitride Powder

A fine white silicon nitride powder was obtained. The proportions of the crystalline phases present depend on the heat treatment, typically heating at 1425°C for 4.25 hours gives 93 % α-silicon nitride.

The elemental analyses, table I, show a good silicon nitride powder stoichiometry, the oxygen content varies enormously if precautions are not taken to avoid oxidation during precursor handling and heat treatment. Carbon content was found to be 0.18 wt.%. Chlorine content was over 1.5 wt.% for some powders, but this was reduced when the heat treatment was made in two steps: the first at 200-250°C for 30 minutes to eliminate NH_4Cl and then at higher temperatures to complete the thermal treatment.

SEM images, Fig.5, show particulates of size under 200 nm, agglomerates as large as 2.4 µm were detected by particle size measurements.

CONCLUSIONS

We have shown that a reaction between an intermediate Si compound and NH_4Cl can take place in the thermal decomposition of an $Si(NH)_2/NH_4Cl$ coprecipitate leading to > 1% Cl content even after treatment at > 1400°C for up to 5 hours.

This Cl impurity level can be substantially reduced if the greater part of the NH_4Cl present is allowed to sublime between 200-250°C, before the reaction is complete (sublimation of NH_4Cl seems to take place at lower temperatures in the presence of $Si(NH)_2$). This has a great practical importance in that the coprecipitation of $Si(NH)_2 + NH_4Cl$ can yield high quality powders, without the necessity of a tedious NH_4Cl washing step, or a high energy consuming reaction-process at liquid NH_3 temperatures or high pressure, and could be carried out in a continuos stirred tank reactor.

The exact mechanism for the reaction between a partially decomposed $Si(NH)_2$ and NH_4Cl is still unclear, further on-line elemental analysis using programmed heating ramps and GC-MS analysis of the decomposition products is hoped to shed further light on the mechanism.

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