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From cyclotetrasilazane $[(CH_3)_2SiNH]_4$ via crystalline silicon nitride imide Si_2N_2NH to α-Si_3N_4

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α-Si_3N_4 is synthesized by an ammonia thermal synthesis using a cyclic oligosilazane, $[(CH_3)_2SiNH]_4$, as the starting material. $[(CH_3)_2SiNH]_4$ reacts in the presence of ammonia at 900 °C and 80 MPa pressure to give silicon nitride imide (Si_2N_2NH). Subsequently, Si_2N_2NH is converted into α-Si_3N_4 by thermal decomposition at 1500 °C and 0.1 MPa nitrogen with the simultaneous loss of NH_3.

Keywords: Silazane, synthesis, thermal, silicon nitride

INTRODUCTION

Due to their outstanding chemical and physical properties, pure silicon nitride (Si_3N_4) ceramics and Si_3N_4/SiC ceramic composites have been considered as suitable materials for heat engine applications and are therefore of great economic interest. These materials possess high thermal stability and oxidation resistance, low electrical conductivity and low thermal expansion coefficients. They are also among the hardest materials which can be produced under atmospheric pressure.

Silicon nitride in its α and β polymorphs was first characterized by X-ray diffraction in 1957.[1] The different industrial processing techniques involve high-temperature synthesis under atmospheric pressure starting from elemental silicon or silica as well as from low-molecular-weight silicon compounds,[2–4] according to the reaction equations [1]–[4].

$$3\,Si + 2\,N_2 \rightarrow Si_3N_4 \qquad [1]$$

$$3\,SiO_2 + 6\,C + 2\,N_2 \rightarrow Si_3N_4 + 6\,CO \qquad [2]$$

$$3\,SiCl_4 + 4\,NH_3 \rightarrow Si_3N_4 + 12\,HCl \qquad [3]$$

$$3\,SiHCl_3 + 4\,NH_3 \rightarrow Si_3N_4 + 9\,HCl + 3\,H_2 \qquad [4]$$

These processes yield mixtures of α-Si_3N_4 and β-Si_3N_4 in different ratios.[2] For the production of Si_3N_4 materials with optimal properties, it is necessary to have a Si_3N_4 starting powder with a high ratio of α-Si_3N_4 ($\alpha/(\alpha+\beta) > 95$ wt %), a low oxygen content (< 1.5 wt %) and negligible contamination from carbon and metallic elements. The present work reports on the synthesis of α-Si_3N_4 with a high α/β ratio starting from easily accessible octamethylcyclotetrasilazane, $[(CH_3)_2SiNH]_4$.

RESULTS

Oligo- and polysilazanes of the general formula $[RSiR'NR'']_n$, where R, R′ and R″ represent H, CH_3 and C_6H_5 respectively, have been intensively studied in recent years with regard to their application as precursors for Si_3N_4-based ceramics.[5–12] The synthesis proceeds by means of the thermal decomposition of silazane. Depending on the pyrolysis atmosphere, either Si_3N_4/SiC composites or pure Si_3N_4 can be produced under atmospheric pressure.[13–15]

$$[CH_3SiHNH]_n \xrightarrow[Ar]{1000\,^\circ C} \frac{n}{4}Si_3N_4 + \frac{n}{4}SiC + \frac{3n}{4}CH_4 + \frac{3n}{4}H_2 \qquad [5]$$

$$[CH_3SiHNH]_n \xrightarrow[NH_3]{1000\,^\circ C} \frac{n}{3}Si_3N_4 + nCH_4 + \frac{n}{2}H_2 \qquad [6]$$

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Table 1 Elemental analysis of OMCTS-derived Si_2N_2NH produced by ammonia thermal synthesis and the resulting α-Si_3N_4 obtained by subsequent heat treatment of Si_2N_2NH at 1500 °C in N_2

Reaction product	Composition (wt %)				
	Si	N	H	O	C
1000 °C: Si_2N_2NH	55.7	39.7	1.1	3.5	<0.2
(Calcd)	56.6	42.4	1.0	0	0
1500 °C: Si_3N_4	n.d.[a]	39.5	n.d.	1.2	n.d.
(Calcd)	60.0	40.0	0	0	0

[a] n.d., not determined.

Generally, cyclic oligosilazanes are produced by the ammonolysis of chlorosilanes according to Eqn [7] representing the synthesis of octamethylcyclotetrasilazane (OMCTS):[16]

$$4(CH_3)_2SiCl_2 \xrightarrow[-NH_4Cl]{NH_3} [(CH_3)_2SiNH]_4 \quad [7]$$

However, due to its low molecular weight, OMCTS cannot be directly pyrolysed by a solid-state reaction to silicon-based ceramics. We have now found that OMCTS reacts completely in an ammonia thermal synthesis under high pressure to crystalline silicon nitride imide (Si_2N_2NH).

$$[(CH_3)_2SiNH]_4 + 2NH_3 \xrightarrow[900\,°C]{80\,MPa} 2Si_2N_2NH + 8CH_4 \quad [8]$$

Si_2N_2NH is considered to be an intermediate compound in the ammonolysis of $SiCl_4$, finally yielding α-Si_3N_4 at $T > 1200$ °C.[3,6] The X-ray diffraction pattern (Fig. 1a) of the reaction product is identical to that of Si_2N_2NH produced by the

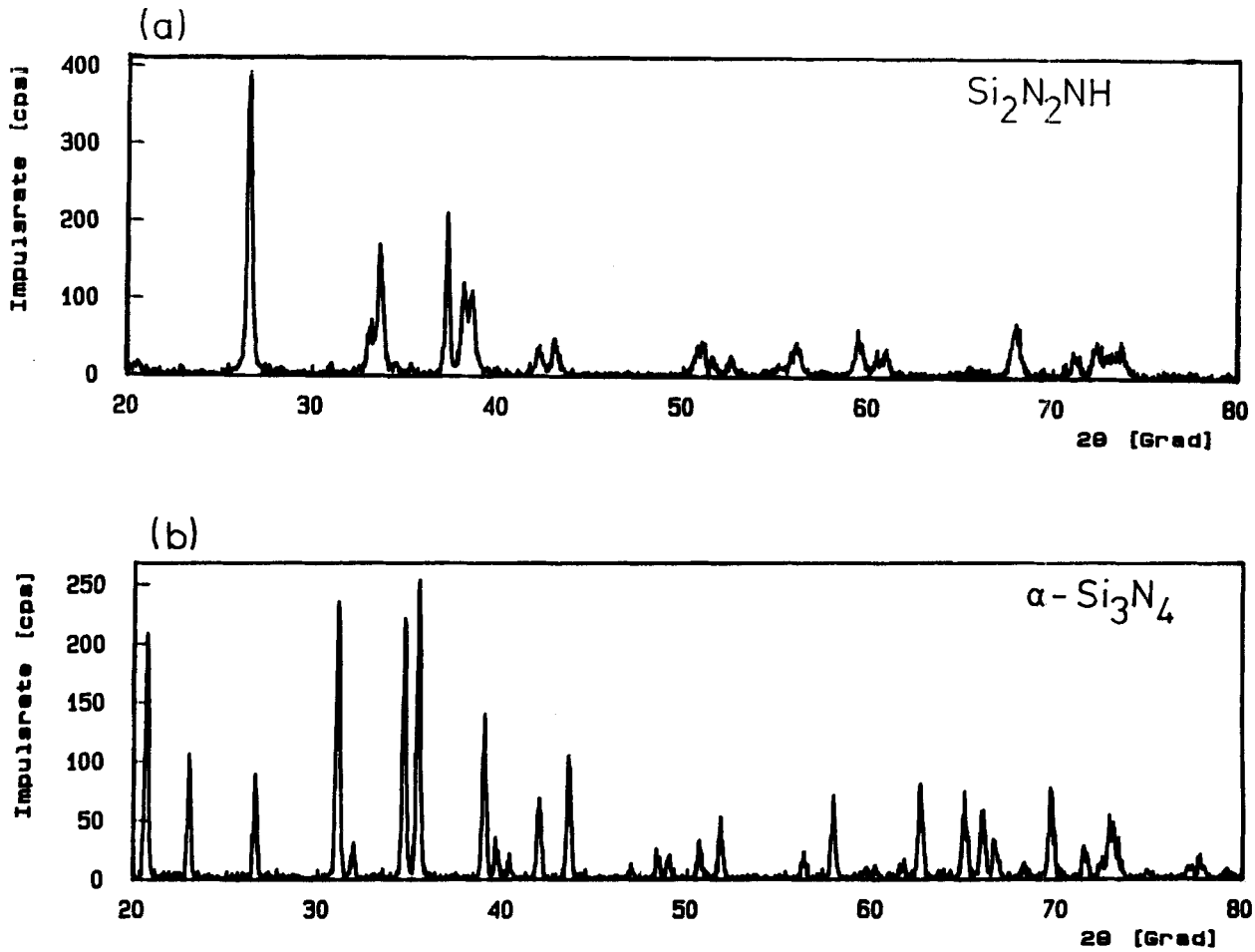

Figure 1 XRD patterns of (a) synthesized silicon nitride imide and (b) Si_2N_2NH heat-treated at 1500 °C in N_2.

reaction of silicon with KNH_2 in ammonia.[17] Optical transmission microscopy with crossed polarizers reveals that the material is completely crystallized.

Data from the elemental analysis of the solid material obtained are given in Table 1 and agree well with the calculated theoretical values for Si_2N_2NH. SEM investigation of crystalline Si_2N_2NH shows the existence of a microcrystalline powder with a spherical particle morphology and an average particle size of approximately 0.15 μm (Fig. 2).

At temperatures above 1000 °C, the Si_2N_2NH reacts to produce α-Si_3N_4 with the simultaneous loss of NH_3 according to the reaction:

$$3\,Si_2N_2NH \rightarrow 2\,\alpha\text{-}Si_3N_4 + NH_3 \qquad [9]$$

In the X-ray diagram of the product heat-treated at 1200 °C, α-Si_3N_4 reflex peaks appear next to those of the Si_2N_2NH. After annealing at 1500 °C, a 94 % yield of α-Si_3N_4 is obtained which can be determined from the X-ray results (Fig. 1b). The absence of X-ray diffraction lines corresponding to β-Si_3N_4 indicates that the $\beta/(\alpha+\beta)$ ratio is less than 2 wt %.[18] The data from the elemental analysis are included in Table 1.

SEM micrographs of the synthesized α-Si_3N_4 show the presence of rod-like crystallites with a particle size of less than 0.7 μm (Fig. 3).

A significant advantage of the synthesis of Si_3N_4 from OMCTS is the application of relatively inexpensive and highly pure starting materials [$(CH_3)_2SiCl_2$ and NH_3]. The oligosilazane OMCTS can be obtained in a very pure form by distillation. In the subsequent ammonia thermal synthesis, gaseous methane (CH_4) results exclusively as the by-product, which can be easily separated from the solid reaction product (Si_2N_2NH). Therefore, as shown in this work, Si_2N_2NH is a suitable precursor for the production of α-Si_3N_4, distinguished by its high phase purity and low oxygen contamination.

EXPERIMENTAL

$[(CH_3)_2SiNH]_4$ (0.01 mol) was heat-treated in a pure NH_3 atmosphere (approximately 80 MPa) for 72 h at 900–1000 °C in an autoclave after humidity and oxygen had been evacuated. The material was subsequently cooled to room temperature and the reaction product separated from excess NH_3 and any resulting CH_4. The crystalline Si_2N_2NH was heat-treated for 5 h at 1200 °C and 1500 °C in a nitrogen atmosphere. At 1500 °C, α-Si_3N_4 is obtained with a yield of 88.6 %, which corresponds to 94 % of the theoretical yield. Phase analysis was conducted by X-ray diffraction with Cu Kα radiation ($\lambda = 150.64$ pm) using a scintillation counting detector. X-ray detection was conducted in steps of 0.03° for 1 s. Photomicrographs of the powder morphology

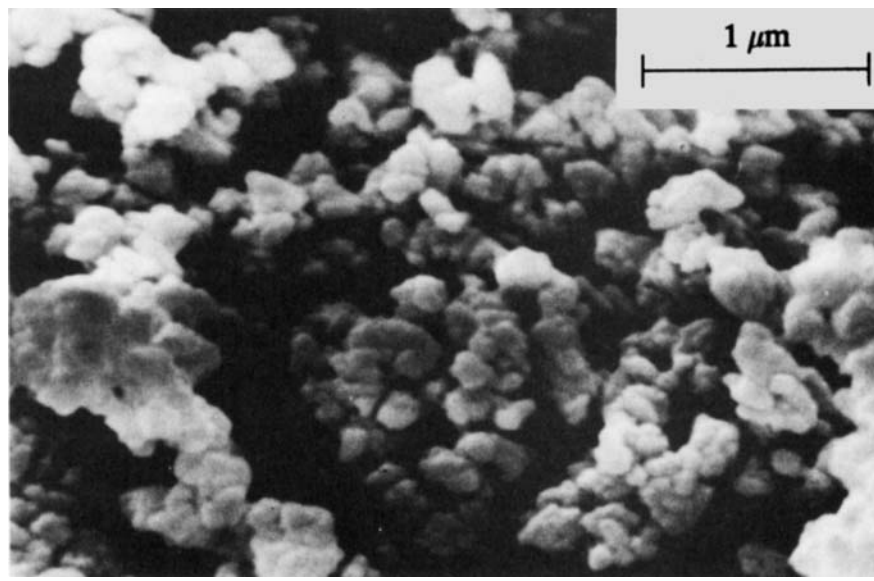

Figure 2 SEM micrograph of microcrystalline Si_2N_2NH.

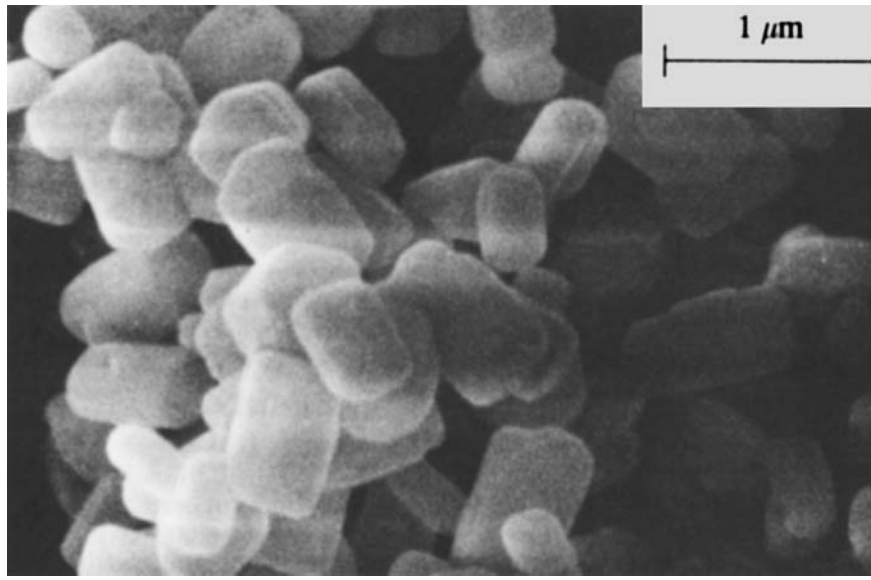

Figure 3 SEM micrograph of α-Si_3N_4 produced.

were taken on a Stereoscan 200 scanning electron microscope (Cambridge Instruments).

The C, N and O contents were determined by high-temperature combustion methods using C,S Analyser Model 244 and N,O Determinator Model TC 436 (LECO Corp., St. Joseph, MI, USA). Silicon was measured by means of optical emission spectrometry with inductively coupled plasma excitation.

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