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# Crystallization of an amorphous silicon nitride powder produced in a radiofrequency thermal plasma

János Szépvölgyi*, Ilona Mohai

*Research Laboratory of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Science,*
*H-1025 Budapest, Pusztaszeri út 59–67, Hungary*

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## Abstract

Crystallization behavior of an amorphous silicon nitride powder produced in an RF thermal plasma by the vapor-phase reaction of silicon tetrachloride and ammonia has been investigated. Effects of annealing conditions such as temperature and duration of heat treatment on the properties of powders were studied. Changes in the chemical and phase compositions, as well as in the morphology of powders were measured and interpreted. Annealing of the amorphous silicon nitride powder at 1450°C for 120 min resulted in a powder of about 80% crystalline phase content with an $\alpha/\beta$ ratio of about 6.5. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* Crystallization; Amorphous $Si_3N_4$ powder

## 1. Introduction

Silicon nitride ceramics of good high-temperature properties are usually produced from pure, high-$\alpha$-$Si_3N_4$ powders of narrow particle size distribution in the micrometer range. However, nanosized amorphous $Si_3N_4$ powders of high surface energies offer considerable advantages [1–3] in terms of sintering rate, because of the availability of crystallization energy.

Silicon nitride powders having a spherical grain structure in the range of 10–100 nm are formed by vapor-phase reaction of silicon tetrachloride and ammonia in RF thermal plasmas. These powders are mainly amorphous with a minor crystalline phase content, due to the very rapid cooling downwards the plasma flame region. In most cases there is a correlation between the oxygen and amorphous phase contents of particular powders [4,5].

The amorphous silicon nitride powders can be processed to dense ceramics in different ways. The traditional processing involves annealing of powders to high-$\alpha$-$Si_3N_4$ materials that can be doped, compacted and sintered at a high temperature. More recently dense ceramics of more than 90% crystalline phase content were produced by the direct hot pressing of amorphous powders without previous annealing [3]. However, application of amorphous thermal plasma powders in the well-established production of advanced ceramics is a topic of outstanding importance both from theoretical and practical points of view. In this respect special attention should be devoted to the crystallization of amorphous powders prior to compacting.

Present knowledge on the solid-phase crystallization of amorphous silicon nitride powders is rather limited. The problems not made clear up to now include, e.g. the onset temperature of crystallization, the changes in the chemical composition and the microstructural developments due to phase transformations.

A crystallization temperature of 1420–1480°C was recommended for the thermal plasma silicon nitride powders in a previous work of the authors [6], although we did not study the effect of crystallization conditions on the properties of powders in detail. Allaire et al. [7] suggested a minimum temperature close to 1500°C for the complete crystallization of amorphous silicon nitride powders. An inverse relationship was found between the temperature and duration of crystallization. Nitrogen in the furnace atmosphere promoted both whisker and $\beta$-$Si_3N_4$ formation. The $NH_4Cl$ content of the starting powder also favored whisker formation, but it had no

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* Corresponding author. Tel.: +36-1325-7896; fax: +36-1325-7892.
*E-mail address*: szepvol@cric.chemres.hu (J. Szépvölgyi).

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effect on the development of β-phase [7]. A fine-grained crystalline, high-α-phase material was obtained by annealing nanosized $Si_3N_4$ powder [8]; the α-$Si_3N_4$ was transformed to a coarser, high-β-$Si_3N_4$ powder by increasing the temperature and duration of heat treatment. A direct transition from the amorphous to β-phase was also observed which makes possible to produce fine-grained β-$Si_3N_4$.

The aim of this work is to establish more precisely the process conditions for the crystallization of an amorphous silicon nitride powder with some crystalline phase content. A special stress is laid on the chemical and phase transformations and morphological changes on crystallization. It should be mentioned that the chemical changes occurring on crystallization of amorphous $Si_3N_4$ powders were not studied and interpreted up to now.

## 2. Experimental

### 2.1. Powder characteristics

The experimental powder was prepared by the vapor-phase reaction of $SiCl_4$ and $NH_3$ in an RF thermal plasma reactor [4]. The as-synthesized powder was subjected to a two-step thermal processing to remove the $NH_4Cl$ and $Si(NH)_2$ by-products formed due to the $NH_3$ excess in the plasma synthesis. The powder was treated in nitrogen at 400°C for 1 h and subsequently at 1100°C for 1 h. In these conditions the by-products decomposed almost completely as it was shown by FTIR analysis.

Characteristics of PSN-O powder subjected to a heat treatment as above are presented in Table 1. For reference a crystalline commercial powder (LC12-SX) is also listed in Table 1. Methods of powder characterization were described previously [4].

The PSN-O powder was mainly amorphous with a crystalline phase content of about 20%. It had a much higher oxygen content and a greater specific surface area as compared to the crystalline LC12-SX powder. The α/β ratios refer to the dominance of α-$Si_3N_4$ phase in the crystalline fractions of both powders, especially in LC12-SX. The SEM investigations showed that the PSN-O sample (Fig. 1) consisted of uniform, spherical particles. However, these particles tend to agglomerate in some extent. The mean particle size as calculated from the specific surface area was 35 nm.

### 2.2. Experimental conditions

The crystallization tests have been performed in a horizontal laboratory furnace in flowing nitrogen at 0.1 MPa. The annealing temperature varied from 1250 to 1500°C, while the annealing time from 30 to 360 min.

The experiments were evaluated by measuring the mass loss on annealing, along with the specific surface area, nitrogen content, phase composition and morphology of crystallized samples.

## 3. Results and discussion

The results of crystallization tests are presented in Table 2. There was a remarkable mass loss on the crystallization of the experimental powder. The mass loss increased with the temperature, as it is shown for the annealing time of 120 min in Fig. 2. Similar runs were

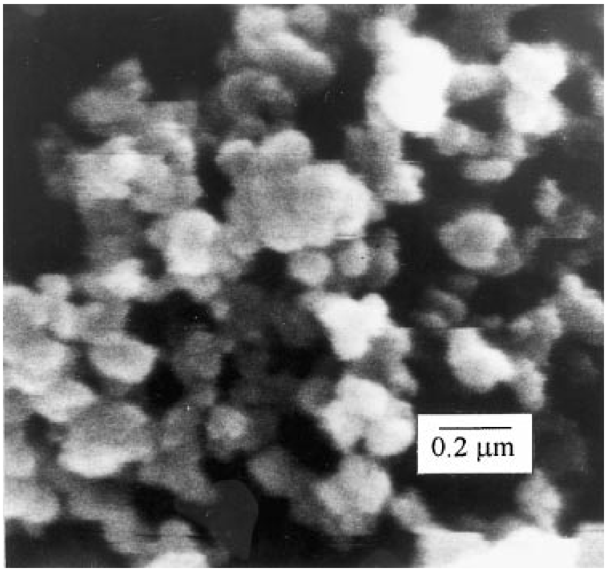

Fig. 1. SEM micrograph of the amorphous $Si_3N_4$ powder.

Table 1
Characteristics of silicon nitride powders

| No. | N | O | Si | C | ΣMe[a] | S[b] | Amorphous fraction (FTIR) | α/β-$Si_3N_4$[c] | |
|---|---|---|---|---|---|---|---|---|---|
| | (at %) | | | | | ($m^2 g^{-1}$) | (%) | FTIR | XRD |
| PSN-O | 52.2 | 5.8 | 42.0 | 0.07 | 0.02 | 54 | > 80 | 4.0 | 4.5 |
| LC12-SX | 55.1 | 1.9 | 42.7 | 0.28 | 0.06 | 22 | < 5 | 32 | 28 |

[a] ΣMe, (Ca + Al + Fe).

[b] S, specific surface area.

[c] α/β ratio (FTIR and XRD, respectively).

obtained for other crystallization times, as well. However, the longer the time, the greater the mass loss was. It is assumed that up to 1350°C the mass loss can be attributed to the removal of residual N–H groups:

$$[Si_2(NH)N_2]_{3n}(s) = 2/3nSi_3N_4(s) + 0.5nN_2(g) + 1.5nH_2(g) \quad (1)$$

However, above 1350°C the following reactions may contribute to the mass losses, as it was concluded after due consideration of powder properties and annealing conditions with a special regard to the oxygen content of nitrogen gas used in the tests:

$$2Si_3N_4(s) + 1.5O_2(g) = 3Si_2N_2O(s) + N_2(g) \quad (2)$$

$$2Si_2N_2O(s) = Si_3N_4(s) + SiO(g) + 0.5O_2(g) \quad (3)$$

$$Si(s/l) + SiO_2(s) = 2SiO(g) \quad (4)$$

$$2Si(s/l) + O_2(g) = 2SiO(g) \quad (5)$$

Eqs. (4) and (5) are probable in the particular case because of the presence of Si–Si–N bonds, as it was established from the XPS analysis of experimental powders [3].

Even the nitrogen content of the experimental powder changed with the temperature (Fig. 3). Up to 1350°C the heat-treated powders had lower nitrogen content than the original PSN-O powder, as it is reasoned by Eq. (1). On the contrary, at crystallization temperatures above 1350°C higher nitrogen contents were measured in the treated powder as compared to the original one. Eqs. (3)–(5) result in an indirect increase of the nitrogen

Table 2
Conditions and results of crystallization tests

| No. | $T$ (°C) | $t$ (min) | $\Delta m/m_o$ (%) | N (at%) | S ($m^2 g^{-1}$) | Amorphous fraction (FTIR) (%) | α/β ratio | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | FTIR | XRD |
| PSN-1 | 1250 | 30 | 0.1 | 52.0 | 50 | 75 | 4.0 | |
| PSN-2 | 1250 | 60 | 1.7 | 52.2 | 46 | 75 | 4.3 | |
| PSN-3 | 1250 | 120 | 1.8 | 51.1 | 37 | 70 | 4.0 | 3.8 |
| PSN-4 | 1350 | 30 | 1.5 | 52.0 | 50 | 75 | 4.6 | |
| PSN-5 | 1350 | 60 | 2.0 | 52.5 | 44 | 70 | 5.0 | |
| PSN-6 | 1350 | 120 | 2.2 | 52.2 | 36 | 65 | 4.1 | 4.0 |
| PSN-7 | 1400 | 30 | 1.8 | 52.5 | 49 | | | |
| PSN-8 | 1400 | 60 | 2.1 | 52.2 | 40 | | | |
| PSN-9 | 1400 | 120 | 3.3 | 53.1 | 32 | 30 | 5.6 | 6.7 |
| PSN-10 | 1400 | 360 | 3.5 | 53.2 | 28 | | | |
| PSN-11 | 1450 | 30 | 4.5 | 52.2 | 40 | 50 | 5.5 | 5.7 |
| PSN-12 | 1450 | 60 | 4.6 | 52.4 | 32 | 40 | 6.1 | 6.5 |
| PSN-13 | 1450 | 120 | 6.0 | 53.4 | 25 | 25 | 6.7 | 7.3 |
| PSN-14 | 1450 | 360 | 6.3 | 55.2 | 20 | 20 | 5.9 | 5.7 |
| PSN-15 | 1500 | 30 | 4.7 | 52.0 | 38 | 40 | 5.4 | |
| PSN-16 | 1500 | 60 | 4.9 | 52.7 | 34 | 30 | 5.5 | |
| PSN-17 | 1500 | 120 | 9.0 | 53.8 | 20 | 20 | 5.9 | 6.1 |
| PSN-18 | 1500 | 360 | 13.1 | 55.0 | 18 | 15 | 5.7 | |

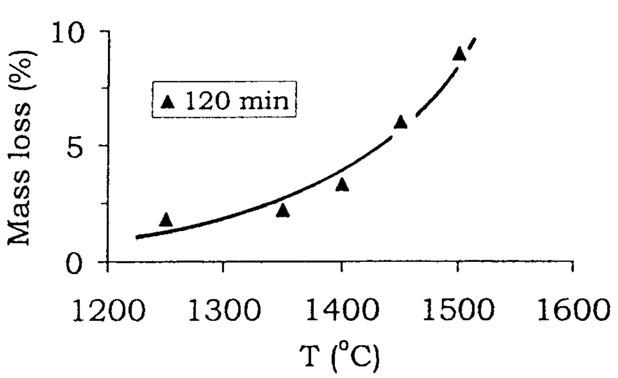

Fig. 2. Mass loss on crystallization as a function of temperature.

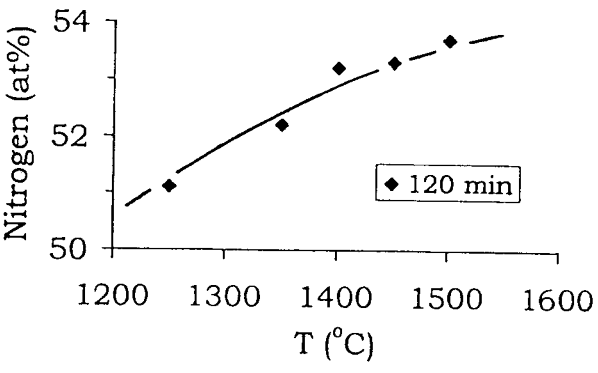

Fig. 3. Nitrogen content of crystallized samples as a function of temperature.

content due to the removal of SiO from the powder. In addition, nitridation of silicon is likely to occur:

$$3\ \mathrm{Si}(s/l) + 2\ \mathrm{N_2}(g) = \mathrm{Si_3N_4}(s) \qquad (6)$$

The amorphous fraction decreased and thus, the powder became more crystalline with rising temperature (Fig. 4). Some crystallization was observed at 1250°C. However, it accelerated above 1350°C. The highest degree of crystallization was over 80% at 1500°C for 360 min with an accompanying mass loss of 13.1%.

The grain structure became coarser on crystallization. The specific surface area decreased from 54 to 20 $\mathrm{m^2\,g^{-1}}$ at 1500°C for 120 min (Fig. 5). The final value is actually equal to that of crystalline LC12-SX powder. Modification of the grain morphology was well detected by SEM investigations, too. Powders consisting of nearly equiaxial grains formed in the crystallization tests. An increased duration of heat treatment led to coarser grain morphologies [Fig. 6(a) and (b)]. Neither whisker formation, nor promotion of β-phase were observed in nitrogen flow which is inconsistent with findings of Allaire et al. [7]. It is very probable that not only the annealing atmosphere and the $\mathrm{NH_4Cl}$ content of powders, but other factors such as crystalline phase content and previous heat treatment of powders, also have an effect on the formation of whiskers. The α/β ratio is considered to be one of the most important characteristics of silicon nitride powders in terms of their processing to dense ceramic materials. In this work the α/β ratio as plotted against the temperature (Fig. 7) has a maximum of about 7 at 1450°C. Below this temperature the amorphous-to-α-$\mathrm{Si_3N_4}$ is likely to be the dominant phase transformation. Above 1450°C, however, both amorphous-to-α and amorphous-to-β transitions are taking place (Figs. 4 and 7). The appropriate crystallization time falls into the range of 120 to 180 min (Fig. 8). The α/β ratio decreased at longer times which is unfavorable in terms of processing to dense ceramics for high temperature applications. In addition, prolongation of the annealing time from 120 to 360 min

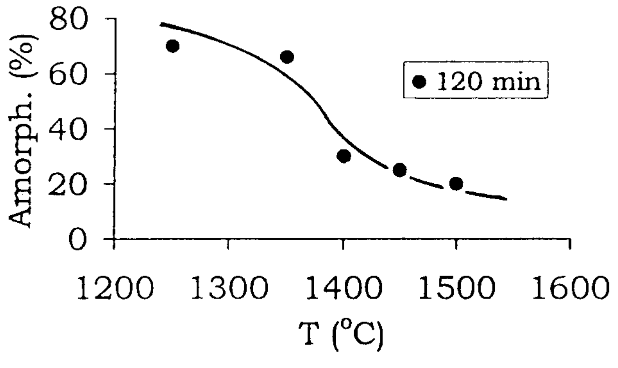

Fig. 4. Decrease of the amorphous fraction against the temperature.

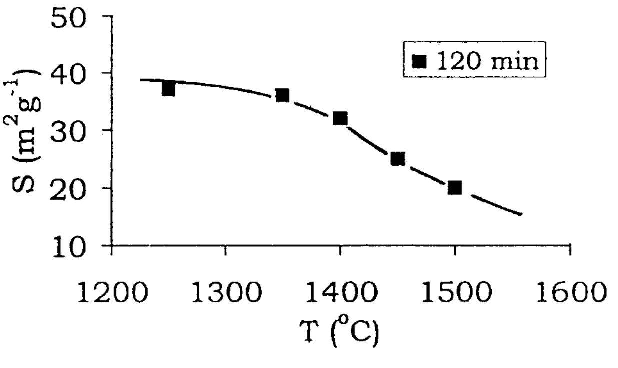

Fig. 5. Specific surface area as a function of crystallization temperature.

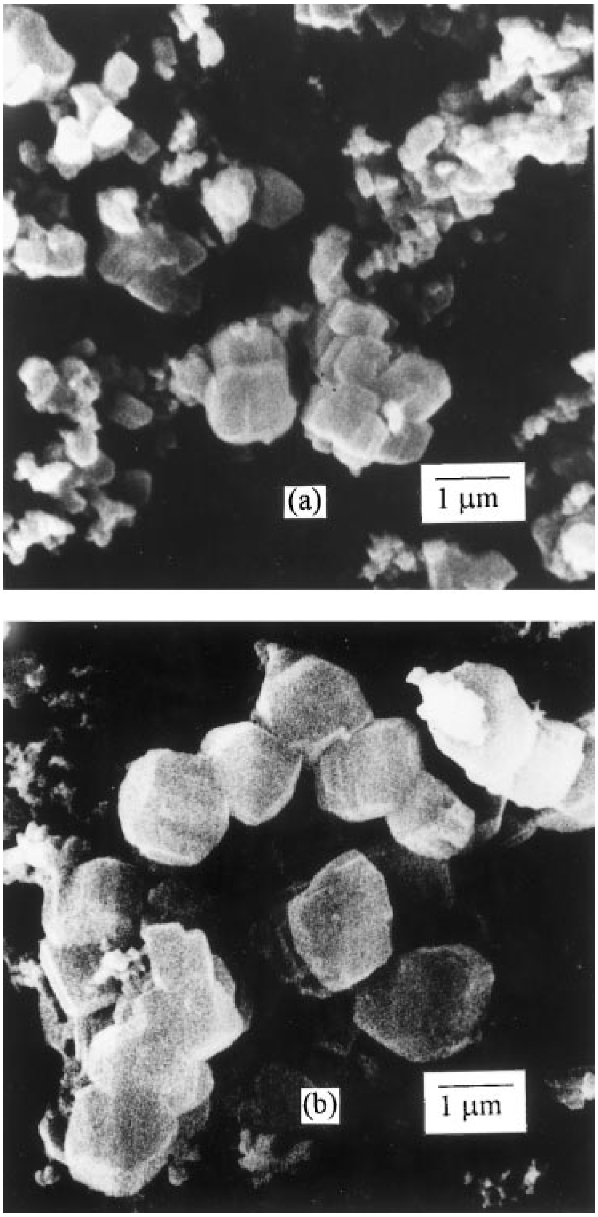

Fig. 6. SEM micrographs of annealed samples: (a) 1450°C, 120 min; (b) 1450°C, 360 min.

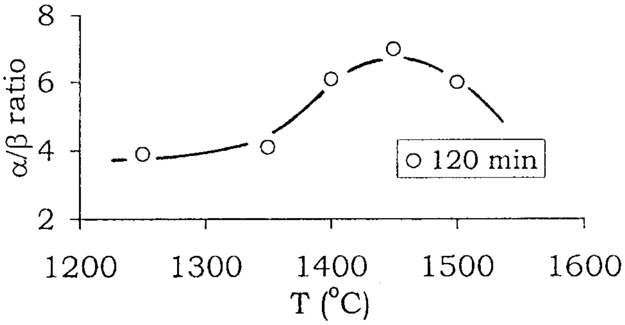

Fig. 7. The α/β ratio as a function of temperature.

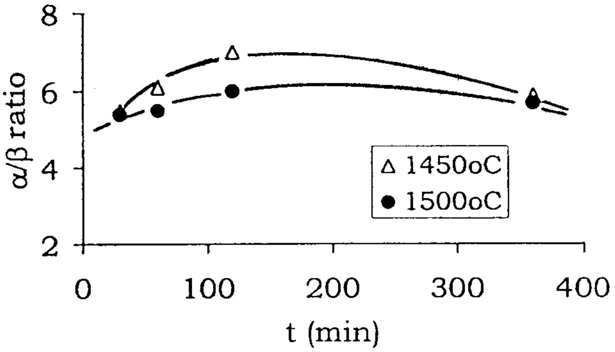

Fig. 8. The α/β ratio as a function of crystallization time.

led to an increase of the mass loss from 9% to 13.1% at 1500°C.

## 4. Conclusions

Properties of a mainly amorphous silicon nitride powder change considerably when it is subjected to heat treatment in nitrogen flow in the temperature range of 1250–1500°C for 30–360 min. The annealing is accompanied with a mass loss varying from 0.1 to 13.1% depending on the temperature and crystallization time. Below 1350°C the mass loss is mainly attributed to the decomposition of residual N–H groups, while at temperatures above 1350°C it is explained by the formation of volatile SiO due to presence of oxygen in the starting powder itself and in the nitrogen purging gas, as well. The nitrogen content slightly increases above 1350°C due to SiO removal and nitridation of silicon. The amorphous-to-crystalline phase transition becomes more significant above 1380°C. The higher the temperature the higher degree of crystallization is achieved. However, the α/β-$Si_3N_4$ ratio has a maximum at 1450°C for 120 min. Further rising of the temperature and crystallization time is not recommended, because the crystallization rate slows down, α/β ratio decreases, while the mass loss rises with the temperature and duration of heat treatment. Therefore, the optimum crystallization conditions of the amorphous silicon nitride powder studied in this work are as follows:

-temperature 1450°C
-duration 120 min.

In these conditions a powder of about 80% crystalline phase content with an α/β ratio of about 7 is produced.

Crystallization is associated with grain coarsening as it is shown by the changes of the specific surface area and also by the results of SEM investigations. Contrary to the previous conclusions, there is no whisker formation in nitrogen atmosphere under the given experimental conditions.

## Acknowledgements

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