# SILICON NITRIDE PRODUCTION: II - ON THE FORMATION OF $Si_3N_4$ SUB-MICRON POWDERS FROM $SiCl_4$ AND $NH_3$ IN AN ARC-PLASMA FURNACE

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## ABSTRACT

Ultafine $Si_3N_4$ powder (50÷150 Å) was prepared in an arc plasma furnace from $SiCl_4$ and $NH_3$. The powder was amorphous and contained $NH_4Cl$ as by-product. By heating in $N_2$, purification and transformation to $Si_3N_4$ was accomplished. Attempts to replace $NH_3$ with $N_2$ were unsuccessful. The experimental conditions and the apparatus are briefly described and discussed.

## 1. INTRODUCTION

$Si_3N_4$ appears to be a promising material for high-temperature technologyes thanks to its good resistance against oxidation, corrosion and thermal shock and its satisfactory mechanical properties (1-6).
$Si_3N_4$ ceramics may be prepared by nitriding Si compacts at 1450 °C in $N_2$ (reaction bonding process), or by hot-pressing $Si_3N_4$ powders (7).
$Si_3N_4$ powders may be prepared by ammonolysis of $SiCl_4$ (8). This process need many steps at temperatures ranging from 0 to 1200 °C.
Finally plasma processes may be an interesting way to produce $Si_3N_4$ powders according to the following single-step reactions:

$$3\ SiCl_4 + 4\ NH_3 \longrightarrow Si_3N_4 + 12\ HCl$$

$$3\ SiCl_4 + 2\ N_2 + 6\ H_2 \longrightarrow Si_3N_4 + 12\ HCl$$

Possibly better-quality products could be obtained in this way as $Si_3N_4$ powders attainable by the ammonolysis process are not satisfactory from a quality as well as from an economic point of view.
In a previous paper (9), plasma process has been examined from a thermodynamic point of view in order to evaluate the best conditions for carrying out the synthesis of $Si_3N_4$ powder.
The conclusions of this previous study may be summarized as follows:
- On the basis of $\Delta G$ and $\Delta H$ variation the use of $NH_3$ is favoured

at high temperature, with respect to the use of $N_2$
- The decomposition of $Si_3N_4$ starts at 1750 °K, beeing almost complete at 2173 °K where $P_{N2}$ reaches the value of one atmosphere. Consequently the synthesis must be carried out at temperatures lower than 2000 and preferably near 1750 °K.
- Since nitriding process with $N_2$ is characterized by slow kinetics, a convenient plasma process must be based on the high reactivity of N atomic and N hydrogenated radicals; these last are available, as transient species, from thermal decomposition of $NH_3$.

Consequently the injected plasma system may have a temperature higher than 2000 °K provided the wall dissipation and the endothermic effect is foreseen to cause a rapid temperature decrease to a value of about 1750 °K.
The aim of this paper is to verify the possibility of carring out the $Si_3N_4$ synthesis by the plasma process evidencing the difference in using $NH_3$ instead of $N_2$ and $H_2$.
To this purpose a special reactor with a mixed A-$H_2$ plasma stream has been used.

## 2. THE APPARATUS

The emplojed apparatus is an arc-plasma reactor arranged in the form of a furnace; its cross longitudinal section is shown in Fig. 1.
The apparatus is made of three parts: a conventional plasma head; an anodic assembly with injection nozzles; a thermally insulated furnace whose core comprises a free expanding graphite tube having the function of principal anode and of reaction zone.
The anode of the conventional plasma head has only an auxiliary function (pilot anode). The furnace is electrically fed with direct current. The plasma stream is emitted from the tip of a cathode made of thoriated tungsten, operating under a little flow of argon.
This gas acts as axial path stabilizing the composite plasma flame. In fact the argon plasma column is injected with hydrogen (through the injection nozzle) in order to have a tubular hydrogen column surrounding the axial argon column.
This composite plasma column is radially distorted and, under the influence of a magnetic field, generated by a electric coil, is rotated with reference to the cilindrical inner surface of a tungsten anode placed on the top of the free expanding graphite tube.

## 3. EXPERIMENTAL RUNS

A particular representation of the electrodic assembly of the plasma-furnace reactor of Fig. 1 is shown in Fig. 2, where the inlets are indicated with numbers (1-5) which are reported in table 1 to describe the entrance of the injected reagents.
Only three runs have been carried out (see table 1); of these the first and the second ones were performed with nitrogen as

nitriding agent, while the third one was performed by nitridation with ammonia.
Only from the third run the $Si_3N_4$ was obtained.
The produced ultrafine powder is shown in fig. 4. The size of the formed powders (white in colour) is in the range 50-150 A.
The product is amorphous but by heat treatment, under nitrogen atmosphere, can be transformed to $\alpha$ - $Si_3N_4$.

## 4. DISCUSSION

The primary $H_2$-A plasma stream is at temperature of 3000 °K.
After the injection of $SiCl_4$ and $NH_3$ the unreacted system shows a temperature of 2200 °K. The mean temperature of the reacted system is in the value of 1650 °K with an intermediate value of 1925 °K.
It is important to consider that the partial pressures of the species present at the complex equilibrium of a $H_2$-$SiCl_4$ starting system are highly affected from the $H_2/SiCl_4$ molar ratio of the same starting system.
In the run 3, thanks to the high molar ratio (17.07), the $SiCl_4$ fed should be present in the system principally as Si species.
Now taking into account that the dwell time in the anodic tube is only 58 millisecond and that the mean temperature is only 1925 °K it appears evident that the local heat transfer will not be satisfied at all, as the presence of a certain amount (22%) of the by-product $NH_4Cl$ demonstrates.
This by-product can be eliminated by heat treatment under nitrogen atmosphere.
Under a so short dwell time it is possible that NH and $NH_2$ species partecipate considerably, together with N, to the synthesis of $Si_3N_4$.
The important condition is that the reacted system is rapidly self quenched at 1650 °K where the $Si_3N_4$ is thermodynamically stabilized.
A higher enthalpic content in the primary plasma stream is considered advantageous for satisfying the energy requirement of the endothermic reaction. It seems that this higher enthalpic content can be obtained by a mixed ternary plasma A-$H_2$-$SiCl_4$.
In this last the sole $NH_3$ should be injected to have the $Si_3N_4$ powder formation.

## 5. CONCLUSIONS

- $Si_3N_4$ can be synthesized with very rapid kinetics at T > 2200 °K by reacting the Si and N species in an homogeneous phase inside the A-$H_2$ mixed plasma stream injected with $SiCl_4$ and $NH_3$.
- The $N_2$ species appears to be inefficient. The active species appears to be N and hydrides radicals attainable by the thermal decomposition of the injected $NH_3$.
- The $Si_3N_4$ powders obtained from the injected reagents ($SiCl_4$ and $NH_3$) are amorphous, ultrafine (50-150 Å) and white in

colour; these powders can be transformed to $\alpha$- $Si_3N_4$ by heat treatment under nitrogen atmosphere.

- As by product $NH_4Cl$ is formed in amount of $\simeq$ 22% in the product. The elimination of $NH_4Cl$ can be attained by heat treatment.
- The synthesis of $Si_3N_4$ from $SiCl_4$ and $N_2$ in a A-$H_2$ mixed plasma stream failed.

Probably better process conditions may be obtained by a direct injection of $NH_3$ into a plasma of A-$H_2$-$SiCl_4$ mixed plasma stream.

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| Run | 1 | | | | | 2 | | | | | 3 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| injected materials (Through → INLETS) | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| A g.mole/h | 53.5 | | | | | 73.61 | | | | | 64.24 | | | | |
| $H_2$ " " | | 129.38 | | | | | | 267.69 | | | | 267.69 | | | |
| $N_2$ " " | | | | | 0.696 * | | 7.85 ** | | | | | | | | |
| $SiCl_4$ " " | | | | 1.047 | | | | | 11.77 | | | | | 15.68 | |
| $NH_3$ " " | | | | | | | | | | | | | | | 21.59 *** |
| Current A. | | | | 120 | | | | 157 | | | | | 75 | | |
| Tension V. | | | | 115 | | | | 125 | | | | | 124 | | |
| Arc Power kw | | | | 13.8 | | | | 19.62 | | | | | 9.3 | | |
| Mean Temp. °K | | | | 3800 | | | | 3200 | | | | | 2500 | | |
| Arc Gas A % MOL. | | | | 29.25 | | | | 2.25 | $N_2$ | | | | 19.35 | | |
| $H_2$ " " | | | | 70.75 | | | | 21.08<br>77.67 | | | | | 80.65 | | |
| Anode Ø Nozzle mm | | | | 18 | | | | 18 | | | | | 18 | | |
| Molar Ratio $\frac{SiCl_4}{NH_3}$ | | | | | | | | | | | | | 0.726 | | |
| $\frac{SiCl_4}{N_2}$ | | | | 1.364 | | | | 1.5 | | | | | | | |
| $\frac{H_2}{SiCl_4}$ | | | | 123.5 | | | | 22.74 | | | | | 17.07 | | |
| Byproducts | traces of β-SiC | | | | | traces of HCN | | | | | 22% of product as $NH_4Cl$ | | | | |
| $SiCl_4$ Transformation % | negligible | | | | | negligible | | | | | | | 84 | | |

* 10% excess ** stoichiometric *** 3% excess

TABLE 1 – PLASMA RUNS FOR THE SINTHESIS OF $Si_3N_4$

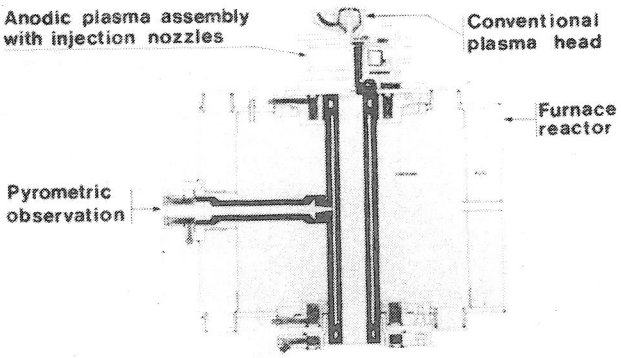


FIG. 1 _ ARC - PLASMA FURNACE

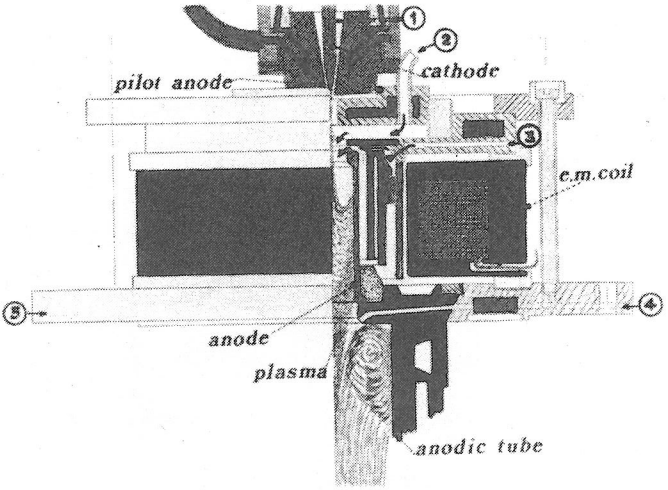


FIG. 2 _ ANODIC ASSEMBLY WITH INYECTION NOZZLES

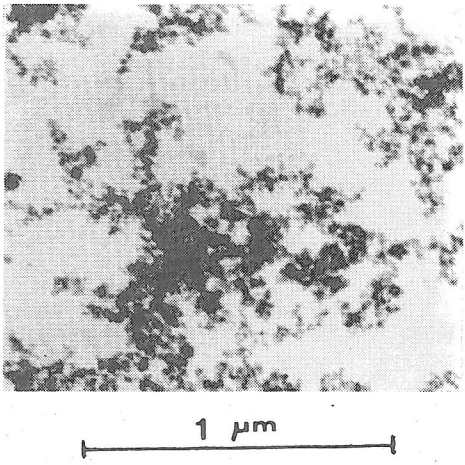


FIG. 3 - ULTRAFINE AMORPHOUS $Si_3N_4$ POWDER