QUALITATIVE ANALYSIS OF SILICON NITRIDE SYNTHESIZED BY AMMONOLYSIS OF SILICON TETRACHLORIDE

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Keywords: Silicon Nitride, Synthesis, Qualitative Analysis.

ABSTRACT:

Silicon nitride powder synthesis, performed by the ammonolysis of silicon tetrachloride, is described in this work. Gaseous ammonia reacts with liquid SiCl₄, at low temperature and inert atmosphere, producing an insoluble ammonolysis product. At a second step, a powder pyrolysis is performed between 1300 and 1500°C, for ammonium chloride removal and Si₃N₄ formation. Phase formation is evaluated by X-ray diffraction. Particle medium size and form is determined by Scanning Electron Microscopy.

INTRODUCTION

Silicon nitride ceramic (Si₃N₄), is strongly considered a important material for use in structural applications, and its performance is severely influenced by modern synthesis processes for high quality powders[1].

The advantages of using this ceramic for several structural applications is related to its high thermal stability up to 1800°C, oxidation resistance up to 1500°C[2], low electrical conductivity, low coefficient of thermal expansion, excellent thermal shock and creep and corrosion resistance in hostile environment[2,3]. Such properties are highly dependent upon microstructural characteristics, originated on fabrication processes[4].

There are three major routes for the preparation of silicon nitride[2]: high temperature reaction of gaseous nitrogen with elemental silicon; gas-phase reaction of ammonia with a chlorosilane (SiCl₄, HSiCl₃, H₂SiCl₂) at high temperatures; reaction of ammonia with SiCl₄ or HSiCl₃ in solution, followed by pyrolysis of the insoluble ammonolysis product and ammonium chloride removal.

The higher free energy formation of NH₃ makes reactions involving this compound more favorable than similar reactions with N₂, considering the higher free energy of formation of NH₃[3].

In the present work, synthesis of Si₃N₄ powder by ammonolysis of SiCl₄, at low temperature in the presence of an organic solvent (hexane) is described. The chemistry reaction has been examined in some detail by Billy[5], et al., Glemser, et al. [6], Mazdiyasni, et al. [3], and Morgan[7, 8, 9], as described.

The Hexane/Silicon Tetrachloride solution reacts with gaseous ammonia, yielding a precipitate of silicon diimide and ammonium chloride, according to the reaction:

\[
\text{SiCl}_4(\text{l}) + 6 \text{NH}_3(\text{g}) \xrightarrow{0^\circ \text{C}} \text{n-C}_6\text{H}_{14} \quad \text{Si(NH)}_2 + 4\text{NH}_4\text{Cl} \quad (1)
\]
The kinetic of reaction is more effective at low temperatures \[^{10}\]. Pyrolysis of obtained product causes NH\(_4\)Cl sublimation \[^{3,11}\], as following:

\[
\begin{align*}
n\text{Si}(\text{NH})_2 (l) & \quad + \quad 4 \text{NH}_4\text{Cl} \quad \xrightarrow{360^\circ\text{C}} \quad 4 \text{NH}_4\text{Cl} + [\text{Si (NH)}_2]_n \\
\end{align*}
\]

The Si(NH\(_2\))\(_2\) polymerizes readily and spontaneously with increasing temperature; its pyrolysis results in two intermediate species before it yields α-Si\(_3\)N\(_4\), according to the reaction (3):

\[
\begin{align*}
6[\text{Si}(\text{NH})_2]_n (l) & \rightarrow 2 [\text{Si}_3(\text{NH})_3\text{N}_2]_n & 650^\circ\text{C} & \rightarrow 3 [\text{Si}_2(\text{NH})_2\text{N}_2]_n & 1200^\circ\text{C} & \rightarrow 2 \alpha\text{-Si}_3\text{N}_4 \\
\quad & \quad - 2\text{NH}_3 & \quad - \text{NH}_3 & \quad - \text{NH}_3
\end{align*}
\]

**EXPERIMENTAL**

Diimide synthesis was performed in a two litters capacity glass Kettle reactor (figure1):

![Kettle Reactor](image)

Fig. 1: Kettle Reactor.

A high purity solution of silicon tetrachloride/hexane was introduced in the reactor, in Argon or Nitrogen atmosphere. A controlled flow of gaseous ammonium is introduced in the above mentioned reactor, starting a very exothermic reaction.

Better results are obtained in a temperature range of 0 and 5\(^\circ\)C, during approximately four hours. The homogenization of reaction media was achieved using a magnetic agitator.

In a second step, the obtained silicon diimide was transferred from the reactor to the alumine and silicon carbide crucibles. This step was performed inside a glove box (figure 2), to avoid diimide contamination by oxygen.
The formed white precipitate was then isolated by the n-hexane distillation under reduced pressure at 25°C. Last step for silicon nitride powder synthesis was the diimide pyrolysis, carried out in high purity Argon or Nitrogen atmosphere, at 1400°C, for two hours. During such heat treatments, ammonium chloride evolution was always observed, at approximately 900°C. Table 1 shows the conditions of diimide silicon pyrolysis, during 2 hours:

Table 1: Pyrolysis conditions

<table>
<thead>
<tr>
<th>Speciment</th>
<th>Temperature</th>
<th>Atmosphere</th>
<th>Crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1450°C</td>
<td>Argon</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>b</td>
<td>1400°C</td>
<td>Argon</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>c</td>
<td>1400°C</td>
<td>Argon</td>
<td>Alumina</td>
</tr>
<tr>
<td>d</td>
<td>1400°C</td>
<td>Nitrogen</td>
<td>Alumina</td>
</tr>
</tbody>
</table>

Preliminary powder characterization was performed by X-Ray diffraction an scanning electron microscopy. For accurate morphologic examination, powder samples were previously prepared by ultrasonic dispersion, during five minutes, using distilled water and “Disperlan”, as dispersion media.

RESULTS AND CONCLUSIONS

Two intermediary compounds has been produced by the ammonolysis of silicon tetrachloride: silicon diimide and ammonium chloride. The compounds were subsequently heat treated in Ar or N₂, obtained previously, are heat treated, and are transformed during heating. Ammonium chloride starts its transformations from solid to gaseous state at 360°C. The subsequent heating causes decomposition of the remanent product, followed by liberation of gas ammonia and hydrogen chloride, aiming crystalline silicon nitride powder production. The possible reaction, in this case, is described as follows:

\[
\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}
\]  

During the pyrolysis, vapor evolution was observed only after 400°C. Very fine grey particles of silicon nitride powder were obtained, occupying a small crucible volume, compared to the starting silicon diimide powder. They were subsequently characterized by scanning electron microscopy and X-ray diffraction.
Silicon Nitride powder $\alpha + \beta$ morphology is shown in the figure 3. High percentage of cylinder particles are observed.

Fig. 3: Morphological analysis of Si$_3$N$_4$ $\alpha + \beta$ to MEV.

Figure 4 shows a X-Ray diffraction to different specimen. The specimen –a peaks present a $\beta$ phase presence, while specimens b, c/d, shows $\alpha$ and $\alpha + \beta$ phases, respectively.

Fig. 4: X-Ray Diffracton of Si$_3$N$_4$ : (a) $\beta$ ; (b) $\alpha$ ; (c) and (d) $\alpha + \beta$.

The $\beta$ peaks appears more frequently above 1400°C (figure 4-a), while $\alpha$ phase is predominant below the same temperature. Very fine $\alpha$ - silicon nitride powders were obtained, using silicon carbide crucible, in Argon atmosphere (Fig 4-b). Apparently, the $\beta$-silicon nitride phase is not nucleated, for the same process conditions.
For alumina crucibles, both phases were observed (figure –c/d), using either Argon or N_2, as furnace atmosphere. Results suggest that oxygen is provided from alumina crucible, during pyrolysis, generating appropriate conditions for α plus β nucleation, therefore, this study is not concluded.

REFERENCES