EXPLORATORY STUDIES ON THE SYNTHESIS OF 
\( \beta \)-SILICON NITRIDE AT LOW TEMPERATURES IN A 
SEALED STEEL VESSEL.

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ABSTRACT
The classical pyro-chemical methods for the production of \( \beta \)-Si\(_3\)N\(_4\) involve high temperature heat treatment of SiO\(_2\) charge in the temperature range of 1673 – 1873 K either in dry nitrogen or in ammonia atmosphere (1-3). These methods consume relatively large electrical energy and kinetic rate of thermal nitridation is slow. In recent years a number of new methods are tried but each one has its own advantages and limitations.

In the present investigation an attempt has been made to prepare \( \beta \)-Si\(_3\)N\(_4\) powders by unconventional in-situ pressure assisted chemical diffusion method. The new method utilizes in-situ gaseous pressures of N\(_2\), H\(_2\) and CO gases which are generated during the thermal decomposition of urea [(NH\(_4\))\(_2\)CO] at a temperature of 923K while heating the charge mixture of silica, magnesium powder and urea in a gas tight sealed S.S container. The heat treatment on the charge was carried out at 923K for 4 h. The thermal diffusion of N\(_2\), H\(_2\), CO, gases in to the silica matrix gave rise to formation of \( \beta \)-Si\(_3\)N\(_4\), at a low temperature of 923 K. The charge after heat treatment was furnace cooled. The cooled product was acid leached in 10.0 % HF. The XRD analysis of the heat treated and leached powder showed peaks of pure \( \beta \)-Si\(_3\)N\(_4\). The reacted product powder showed presence of nearly 90 vol % \( \beta \)-Si\(_3\)N\(_4\) and 10 vol%, un reacted mass. The Malvern particle size analysis of product showed that the majority of the particles have average diameter of 53.0 \( \mu \)m.

Introduction
In recent years novel synthesis routes such as combustion synthesis, shock wave synthesis, mechano activation, chemical vapor deposition and thermal plasma methods are tried for the production of ceramic nitrides and carbides. The conventional methods for the production of ceramic compounds namely Si\(_3\)N\(_4\), AlN, TiN, etc, require temperatures of the order of 1573 - 1873 K in nitrogen or ammonia atmospheres,
hence considerable electrical energy is spent in the production of these compounds. The synthesis of Si₃N₄ from powdered silica either in nitrogen or ammonia atmosphere involves gas-solid reaction and therefore formation of product layer and its gaseous permeability influences the reaction rate and the physical parameters like powder porosity, particle size, shape, size distribution and thermodynamic parameters like gas pressure, temperature, activity of the reactant collectively influence the reaction rate. The chemical nature of raw material i.e., nature of chemical bond present in the raw material (ionic or covalent) profoundly influence the rate of conversion of raw material in to desired product. In the methods described above pressure parameter is held constant which is usually kept at atmospheric pressure.

In the new method, proposed by the authors an attempt has been made to generate in-situ N₂ and H₂ gas pressures by the decomposition of urea present in raw material mixture of silica, magnesium and urea which is enclosed in a perfectly sealed stainless steel vessel. The dissociation of urea at a low temperature of 923 K generates sufficient enough nascent and reactive N₂, H₂ and CO gases which increases the total pressure of the in-situ gases to nearly 50 to 60 atmospheres. (calculated on the basis of Avagadro’s law). The presence of magnesium metal in raw material charge induces metallo-thermic reduction of SiO₂ to SiO and Si, which subsequently helps in the formation of Si₃N₄, phase. The N₂, H₂ and CO gas molecules diffuse in to nascent silicon particles under the influence of pressure and temperature which gives rise to formation of β-Si₃N₄ at low temperatures and by product CO₂, NO₂, H₂O etc. The pressure generated by the liberating gases from urea helps in the reduction of silica and in cracking of product layer on the reactant. The present investigation describes the synthesis of β-Si₃N₄ through pressure assisted chemical diffusion process.

**Experimental**

The SiO₂ powder of 99.2 % purity, Mg metal powder of 99.9% purity and urea of 99.2 % purity were mixed in agate mortar pestle in the required weight proportions. The homogeneously mixed powder mass consisting of 6.0 g of silica, 9.0 g urea and 2.4 g of magnesium was transferred to cylindrical stainless steel reactor having an I.D of 25.0 mm and 50.0 mm depth with overall free volume of 25 CC. The sketch of the pressure reactor is shown in Fig -1. After putting the charge, mouth opening of the reactor was closed in air tight manner by placing stainless steel plug in the opening and welding the same. The vessel consisting of charge was heated in a pit type Kanthal wire wound electrically resistance heated furnace to a temperature of 923K for 240 minutes during which time N₂ gas pressure was
developed during heating to peak temperature.

After high temperature soaking reaction vessel was taken out from the furnace with the help of tongs’ and cooled in open air. After drilling a 6.0 mm hole in the top lid, the reacted powder was poured into a glass beaker. The reacted powder mixture was leached in 10.0% HF for 180.0 minutes, the leached powder was rinsed with deionised water and dried at 383K for 120.0 minutes. The dried powder was characterized for lattice type using Phillips model No: pw 347 XRD spectrometer and graphite monochromator. The XRD spectrum of the reacted mass is shown in Fig-2. The particle size distribution of the product powders was analyzed by Malvern particle size analyzer. The size distribution powder is shown in Fig -3.

**Results and discussions**

The XRD spectrum (Fig-2) of the reacted and leached powder shows XRD peaks at 'd' values of 23.17°(3.83Å), 26.47°(3.36 Å), 33.6° (2.66 Å), 35.07°, (2.55 Å) 36.53° (2.45 Å), 40.57° (2.22 Å), 43.25°(2.08 Å), 49.94°(1.82 Å), 52.46°(1.74 Å), 59.13° (1.5568 Å), 61.0°(1.51 Å), 66.4°(1.433 Å), 76.8°(1.24 Å), due to presence of β-Si₃N₄ which indicates massive transformation of silica to β- silicon nitride under the influence of high partial pressures of N₂, H₂ and CO and an XRD peak at 46.3° (1.9593 Å), shows presence of trace amounts of Mg₃N₂ and a peak at 62.1° (1.49 Å) shows presence of small amounts of MgO phase. The process gives high product yield (of nearly 70%). The formation of silicon nitride compound can be attributed to, i)magnesio-thermic reduction of silica by magnesium powder to silicon powder particles .ii)decomposition of urea to N₂, H₂, CO gases and diffusion of these gases in to silicon or silicon monoxide particles by gas -solid diffusion at 923 K which causes accelerated chemical reactions such as,

1) < SiO₂ > + 2 < Mg > = < Si > + 2 < MgO >
2) 2 < SiO₂ > + 2< Mg > = 2 < SiO > + 2 < MgO >
3) <(NH₄)₂CO > = (N₂ ) + 4 ( H₂ ) + (CO )
4) 2 <SiO> + 4 (H₂) = 2(H₂O) + 2< Si >
5) 3. < SiO₂ > + 6 < Mg> + 2 ( N₂ ) = < Si₃ N₄ >
   + 6 <MgO>
6) 3 < Si > + 2(N₂) = < Si₃ N₄>
7) 3 < SiO > + 2 ( N₂ ) = < Si₃ N₄ > + 3/2 (O₂)
8) <SiO> + (CO) = <Si > + (CO₂)

The combination of the above mentioned chemical reactions taking place at 923 K are the probable cause of formation of β-Si₃N₄ phase. Since these chemical reaction take place at low temperatures of 923 K, considerable heat energy can be saved in the synthesis of β- Si₃N₄ material. Fig-3. shows size distribution of purified β- silicon nitride powders. The average diameter of the majority of
Conclusion:

The pressure assisted chemical diffusion is effective in the formation of $\beta$-Si$_3$N$_4$. The XRD investigations confirm the formation of $\beta$-Si$_3$N$_4$ as a major phase. The process is economical.

2) It is possible to synthesize $\beta$-Si$_3$N$_4$, from a mixture of SiO$_2$, Mg, and (NH$_4$)$_2$CO, raw material mixture at a relatively low temperature of 923 K.

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References


Fig 1. Stainless steel pressure vessel,
1) Cylindrical ss container, 2) raw material charge,
3) S S plug, 4) Weld joints

Fig. 2 XRD spectrum of purified silicon nitride product
Fig 3. Particle size distribution curve of silicon nitride particles