Synthesis of Si$_3$N$_4$ in the nanopores of silica gel matrix by in-situ generation of nitrogen

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ABSTRACT

Nanosized silicon nitride has been prepared reacting tetraethyl-orthosilicate, n-decanol and ammonium nitrate at temperatures between 800 and 1000^{0}C under argon atmosphere. An innovative technique has been used for the synthesis of silicon nitride by in-situ generation of nitrogen through a sol-gel route. The structure and phase composition have been characterized by infrared spectroscopy, transmission electron microscopy and X-ray diffraction. The average particle size of Si$_3$N$_4$ was in the range 6-12nm under various reaction conditions. The probable reaction mechanism of Si$_3$N$_4$ formation is also deduced.   © 2008 Trade Science Inc. - INDIA

INTRODUCTION

Silicon nitride is a wide band gap($\approx$5.3eV) semiconductor as well as a ceramic material owing to its high-temperature strength, lightweight and good resistance against thermal shocks as well as oxidation[1-3]. This material may potentially be utilized for automotive engine wear parts, such as valves, turbine blades, vanes, buckets and cam followers which operate at high temperature and, thereby, increasing the efficiency of the engine. Silicon nitride having a one-dimensional nanostructure has recently attracted much attention due to its potential application in micro-electronic devices as well as nanostructured composite materials. These materials have revealed unique optical, electrical, magnetic and mechanical properties, each of which differ from that of the bulk materials. Silicon nitride is rather an expensive material, but its performance to the cost-benefit ratio is excellent in the field of applications. If compared to engineering materials, nanosized silicon nitride has a long life and is very reliable with low maintenance operation[4].

The synthesis of silicon nitride powders and nanocomposites is described in some previous publications. Si$_3$N$_4$/BN composites with laminated structures were prepared and investigated through the composition control and structure design. To further improve the mechanical properties of the composites, Si$_3$N$_4$ matrix layers were reinforced by SiC whiskers, and BN separating layers were modified by adding Si$_3$N$_4$ or Al$_2$O$_3$. The results showed that the addition of SiC whiskers in the Si$_3$N$_4$ matrix layers could greatly improve the apparent fracture toughness, at the same time keeping the higher bending strength of the composites. Additions of

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50wt% Al_2O_3 or 10 wt% Si_3N_4 to BN interfacial layers had a beneficial effect on the strength and toughness of the laminated Si_3N_4/BN composites[5].

Porous silicon nitride with macroscopically aligned channels was synthesized using a freeze-drying process. Freezing of a water-based slurry of silicon nitride was done, while unidirectional controlling the growth direction of the ice. Pores were generated subsequently by sublimation of the columnar ice during freeze drying. By sintering this green body, a porous silicon nitride with high porosity was obtained and its porosity was controllable by the slurry concentration[6].

A chemical process for the fabrication of Si_3N_4/BN nanocomposite was devised to improve the mechanical properties. Si_3N_4/BN nanocomposites containing 0 to 30vol% hexagonal BN(h-BN) were successfully fabricated by hot-pressing Si_3N_4 powders, on which turbostratic BN(t-BN) with a disordered layer structure was partly coated[7].

A method to synthesize high-density silicon nitride nanowires directly from the silicon substrates via a catalytic reaction under ammonia or hydrogen flow at 1200^0C was described in[3]. Gallium, gallium nitride, and iron nanoparticles deposited on the silicon substrate were used as catalysts. Gallium nitride could act as a nitrogen source under hydrogen. The average diameter of the nanowires was of 40nm and their length was about of 300μm. The synthesized silicon nitride nanowires consist of a defect-free single crystal grown with various growth directions.

The SiC nanoparticles are formed by in situ reaction between an oxide phase on the surface of Si_3N_4 powder and carbon, which was coated on Si_3N_4 powder by thermal decomposition of methane gas[8]. The advantages of the process are as follows : Easy to process, low cost, fine SiC particles less than 50nm in diameter, and direct bonding between SiC particle and Si_3N_4 grain at the grain boundary without a glassy phase. Another advantage of this method is the applicability of surface-oxidized Si_3N_4 powders, which were generally regarded as deteriorated powders. The present carbon coating method used an oxidized powder to produce high quality Si_3N_4 ceramics.

SiC-Si_3N_4 composite of ultrafine particles with various compositions were prepared by a laser-induced gas-phase reaction[9]. The particles were heat-treated

in Ar or Ar+N_2 atmosphere in the temperature range of 300-1773K. Ultrafine particles of SiC-Si_3N_4 composites consist of SiC, metallic Si and Si_3N_4, depending on the nitrogen and carbon contents. They are thermally stable up to 1573K in Ar without significant changes in the crystalline phase and microstructure, but the nitrogen-containing SiC phase decomposes into SiC, Si and Si_3N_4 accompanied by a remarkable increase in the particle size above 1773K. However, a small amount of nitrogen in the atmosphere could suppress the phase transformation and particle size growth.

The compressive deformation behavior of a 4032 aluminum alloy matrix composite reinforced with 20vol% Si_3N_4 whiskers was investigated at strain rates of 0.016-1.0s^{-1} and at elevated temperature[10]. The deformation temperatures were below and above the solidus temperature of the composite, which was determined by differential scanning calorimetry. It was found that the flow stress of the composite decreased with increasing compressive temperature. The morphology of the eutectic Al-Si alloy was found to play an important role in the compressive deformation behavior of the composite. In addition, there are interfacial reactions between the matrix and Si_3N_4 whiskers due to segregation of the alloy elements near the matrix/reinforcement interfaces.

Nanocrystalline $Lu_2Si_2O_7$ phase was synthesized by the sol-gel method. The formation of $Lu_2Si_2O_7$ occurred at very a low temperature(1050^0C), in comparison with the solid-state reaction between Lu_2O3 and SiO_2. The $Lu_2Si_2O_7$ coat was formed at the surface of the Si_3N_4 substrate by sol-gel method[11]. As $Lu_2Si_2O_7$ has a thermal expansion coefficient very close to that of Si_3N_4, a crack-free, dense (environmental barrier coating) layer could be formed over Si_3N_4 ceramics by coating with $Lu_2Si_2O_7$ precursor sol. Furthermore, as the coating layer was dense, it would certainly protect the substrate from oxidation and corrosive environments.

The conventional method of preparation of silicon nitride is the carbothermic reduction of silica, followed by a nitriding reaction at temperatures higher than 1300^0C [3]. Since the mixtures are in the solid state the homogeneity of the product obtained is not good. Moreover, the size of SiO_2 and carbon particles are large, thereby makes slow the kinetics of thir interaction. So,

if the particle size of SiO_2 and carbon can be reduced down to nanometric region, the kinetics of the carbo thermal reduction will be enhanced. Consequently, the size of the homogenized Si_3N_4 produced is in the nanometric range, and may further influence the thermodynamics of the reaction.

The Sol-gel route is one of the most versatile routes for the preparation of nano- ceramics or nanopowders. Silica gel particles obtained through the sol-gel route were of nanometric in size and formed the interconnected nanopores. Ganguly et al.[12] reported that starch, used during sol-gel process were presented in the nanopores which on subsequent heating at 300^0C in nitrogen atmosphere could provide very fine carbon particles, homogeneously distributed in the nanopores of the gel. Homogeneously mixed SiO2 and carbon nanometric particles could at higher temperature in N_2 atmosphere with formation of Si_3N_4 in the pores of the gel as follows

$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO$

Before the above mentioned reaction starts nitrogen has to diffuse from outside into the gel matrix via the nanopores. So, naturally the process is slow and the formation of Si_3N_4 starts from the outer surface of the gel matrix. This leads to a wider distribution in the size of the Si_3N_4 particles obtained.

The present investigation has been taken up to overcome the previous limitation by in- situ generation of N_2 all over the silica gel matrix, which contains extremely fine carbon in the nanopores of the gel. Therefore, the formation of Si_3N_4 all over this matrix starts instantly. Since the diffusion of N_2 is not necessary here, the process is much faster. The reaction occurs simultaneously throughout the bulk of the material and the distribution of particle size could be much narrower and more uniform. The following methodology has been adopted for the preparation of Si_3N_4 nano-composite by *in-situ* generation of nascent nitrogen. The present experiments were also performed according to a statistically planned technique of experimental design[13-15]. Advantage of this technique is yielding optimum conditions by performing smaller number of experiments. Here a regression equation is formed, from which the influence of each process variable and its relative influence on the process can be readily assessed. Besides this, the influence of the interaction of the effect of two or more variable can be interpreted, which is impossible in classical experiment.

EXPERIMENTAL

1. Synthesis

Ammonium nitrate and n-decanol containing SiO_2 were prepared by the sol-gel route. Tetraethyl-orthosilicate (TEOS, E.Merck 99.9%), ammonium nitrate (E.Merck) and n-decanol (E.Merck) were used as precursors of Si, N and C, respectively.

A solution of tetraethyl-orthosilicate and ethanol at ice-cold temperature was prepared under constant stirring. A solution of ethanol, double distilled water and NH_4NO_3 was added dropwise to the former solution, which was followed by the addition of an ice-cold solution of n-decanol, H_2SO_4 and HNO_3 under constant stirring. The resultant sol was allowed to get gel at room temperature in a vessel covered by paraffin to avoid moisture from the atmosphere. After about seven days, a transparent gel was obtained. The dried gel was heated at 120^0C. The theoretical molar composition of the solid gel prepared was TEOS: C_2H_5OH : H_2O:$C_{10}H_{21}OH$: NH_4NO_3: H_2SO_4: HNO_3 =1:3:1:1:3:0.25:0.1. This low-temperature-treated gel was subsequently heat-treated at temperatures of 800, 900 and 1000^0C .

2. Characterization technique

Infrared spectra were obtained in a Perkin-Elmer 833-IR spectrometer with KBr optics. The samples were previously diluted with KBr (1/20 wt%) and the spectra were recorded in the range 4000-200cm^{-1} at room temperature. The spectrum of KBr powder was used as background.

The heat-treated samples were ground in an agate mortar passed through a 300-mesh sieve. The X-ray diffraction (XRD) patterns of the powder samples were recorded using a Bruker D-8 Advance device working with $CuK\alpha$ radiation in a continuous scan mode in the diffraction angle range $2\theta= 20-80^0C$ with a 0.02 sampling interval and 0.1s scan rate.

The ground samples were dispersed in methanol. A drop of methanol with suspended particles was deposited on to the carbon-coated grids. This carbon-coated grid was investigated by transmission electron micros-

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copy (TEM; Hitachi H600) to observe the size and morphology of the particles obtained and elemental analysis was carried out by energy dispersive x-ray analysis spectroscopy (EDX).

3. RESULTS AND DISCUSSION

1. Infrared feature

The infrared (IR) spectrum of room temperature (RT)-dried gel is presented in Fig. 1a. SiO_2 shows IR bands at 458, 808, 954, 1083, 1160 and $1635cm^{-1}$. According to the literature data these bands are ascribed to Si-O-Si asymmetric bending, Si-OH stretching, (TO) mode of Si-O-Si asymmetric stretching and (LO) mode of Si-O-Si asymmetric stretching[16].

Besides the bands observed in the SiO_2 spectrum, an additional IR band was present at $1050cm^{-1}$ in the spectrum of (RT)-dried gel. This band is assigned to –CH_3 asymmetric and /or –CH_2 groups that can be associated with n-decanol. But this band is absent in the spectrum of the gel heated at 120^0C (Figure 1b). From this observation it was concluded that n-decanol was decomposed at 120^0C in the presence H_2SO_4 and HNO_3, and generated extremely fine carbon particles in the pores of the gel matrix. The important bands appeared at $3140cm^{-1}$ (gels dried at RT) and $1385cm^{-1}$ (gels heated at 120^0C). This clearly indicates that NH_4NO_3 (the source of N_2) remained intact in the pores of the gel matrix.

In the IR spectra of the gel heat-treated at 800, 900 and 1000^0C for 5min in argon atmosphere (Figure 1c), the absence of the 3140 and $1385cm^{-1}$ bands corresponding to NH^{4+} and NO_3^- are noticed[17]. It can be concluded that NH_4NO_3 decomposed all over the matrix simultaneously generating nascent nitrogen, which reacts with SiO_2 and fine carbon, to form Si_3N_4 nanoparticles. In all these spectra, new vibrational bands in the range of $800-1100cm^{-1}$ appeared. This band was ascribed to the Si-N stretching vibration mode of Si_3N_4 [3,18].

2. Evaluation of the crystallographic property

The crystalline phases of the heat-treated powders were identified by X-ray powder diffraction of the different samples heat-treated at 800, 900 and 1000^0C for 5min in argon atmosphere. The crystallite size of the
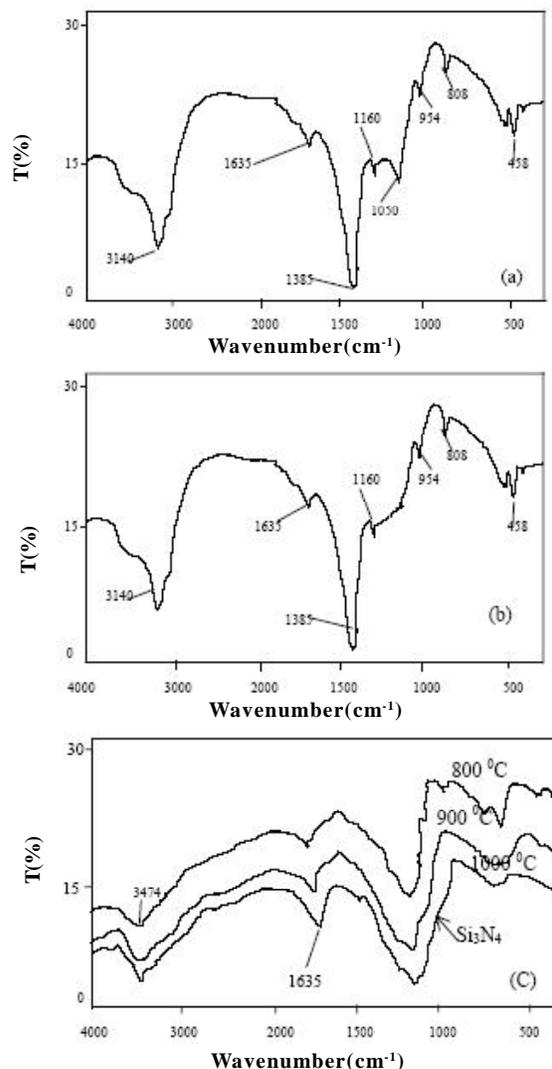

Figure 1: IR spectrum in the 4000-200cm⁻¹ region of the samples studied: (a) gel dried at room temperature (b) 120⁰C and gel heat-treated at (c) 800, 900 and 1000⁰C

nanoparticles was calculated using Scherrer's equation

$$D = K\lambda / \beta \cos\theta$$

where K = 0.9; D is the crystallite size, λ is the wave length of the CuKα radiation and β is the corrected peak width at the half maximum in intensity. Figure 2a shows typical X-ray diffraction patterns of the gel heat-treated at 800 ^0C for 5 min in argon atmosphere. The reflections appeared are attributed to the different crystallographic planes of Si_3N_4 [3,15] These crystallographic planes indicate the presence of a-Si_3N_4 with an average particle size of 6.5nm. For comparison, the spectrum of the gel produced without NH_4NO_3 (Figure 2b) and heat-treated at 800^0C for 5min in N_2 atmosphere was studied. No peaks were observed in

the XRD diagram (Figure 2b) indicating the absence of Si_3N_4 crystals. From this observation it is possible to conclude that NH_4NO_3 is necessary to generate nascent nitrogen in the pores of the gel matrix for the synthesis of Si_3N_4. Figure 2c shows the diffraction pattern of the gel with NH_4NO_3, heat-treated at 900^0C for 5min in argon atmosphere. Some new peaks appeared and a few peaks disappeared when compared to Figure 2a. From this observation it is clear that $\beta\text{-}Si_3N_4$ is formed which is more predominant. Figure 2d shows also the diffraction pattern of the gel containing NH_4NO_3 heat-treated at 1000^0C for 5min in argon atmosphere. By comparison with the standard d_{hkl} values it was observed that only $\beta\text{-}Si_3N_4$ was formed at 1000^0C. The average particle size of $\beta\text{-}Si_3N_4$ was found to be 9 and 12nm at 900 and 1000^0C, respectively.

Figure 3 shows the TEM images of the gels synthesized with NH_4NO_3 and heat-treated at 800, 900 and 1000^0C in argon atmosphere for 5min. From the TEM images the computed size of the Si_3N_4 was found to be respectively 6, 9 and 12nm with the heat-treatment temperatures form 800 to 900 to 1000^0C. Moreover, it was observed that the synthesized Si_3N_4 nanoparticles were uniformly distributed in the silica gel matrix.

3. Mechanism of Si_3N_4 formation

It is possible to consider the following mechanism of the process investigated. Decanol is decomposed by sulfuric acid and nitric acid to generate extremely fine carbon, at a temperature of about 120^0C. This results in the generation of extremely fine carbon in the pores of the silica gel matrix, according to the following reaction:

$$C_{10}H_{21}OH \xrightarrow[\text{HNO}_3]{\text{H}_2\text{SO}_4} C$$
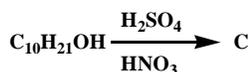
However NH_4NO_3, remained intact in the pores of the gel matrix, which is seen in the IR spectrum. The addition of sulfuric acid serves two purposes. The first and more obvious one is to aid the direct formation of the compound with decanol and its dispersal into the solution, the latter being immiscible in the solution. Secondly, it helps to decompose decanol at 120^0C to generate extremely fine carbon in the pores of the gel matrix. HNO_3 plays an important role by increasing the solubility of the NH_4NO_3 in the solution. Therefore, a homogeneous fine solution was obtained.
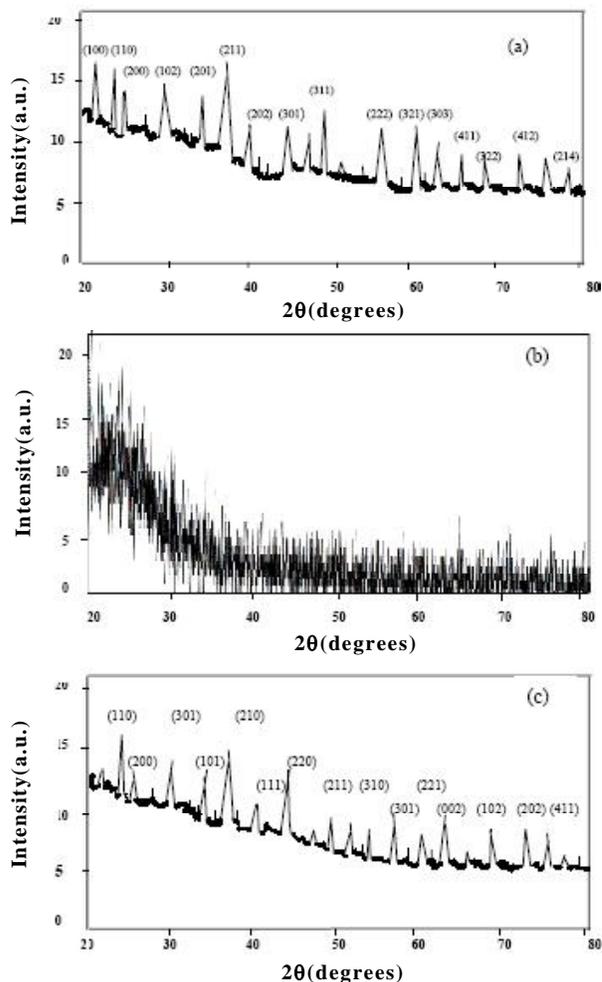

Figure 2: Evolution of the XRD pattern of samples as a function of temperature:(a) 800⁰C, (b) 800⁰C (without NH4NO3) , (c) 900⁰C and (d) 1000⁰C

When this low-temperature(120^0C)-treated gel samples are heat-treated at high temperature of 800, 900 and 1000^0C for 5min in argon atmosphere, NH4NO3 decomposed all over the matrix; simultaneously generating nascent nitrogen that takes part in the formation of Si3N4 according to the following chemical reactions:

NH4NO3 + 2C = 4N + 2CO2 + 2H2O
3SiO2 + 6C + 4N = Si3N4 + 6CO
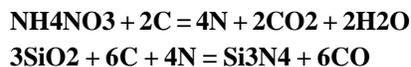
Thus the synthesis of Si_3N_4 occurs all over the matrix, right from the beginning.

The experimental data obtained from XRD have been analyzed on the basis of statistically computations according to the design of the experiments. In the design of experiment the results were obtained by delib-
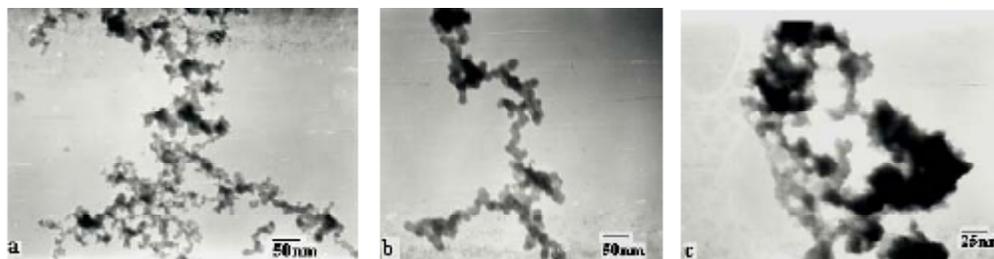
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Figure 3 : TEM images after heating at different temperatures: (a) 800^{0}C, (b) 900^{0}C and (c)1000^{0}C

TABLE 1: The variable process parameters and their selected range

Sl. no	Variable name	Variable code (Zj)	Max. value Z_j^{max}	Min. value Z_j^{min}	Z_j	ΔZ_j	X_j^{max}	X_j^{min}	$-X_j$
1.	NH_4NO_3	Z_1	300 % excess	100 % excess	200% excess	100	+1	-1	0
2.	Decanol	Z_2	25% excess	25% less	stiochio metric	50	+1	-1	0
3.	Tempe-rature	Z_3	1000^{0}C	800^{0}C	900^{0}C	100	+1	-1	0

erately varying the experimental parameters like the percentage of ammonium nitrate, percentage Decanol and reaction temperature in argon atmosphere.

4. Statistical design

In the present experimentations, variables are controlled at two levels factorial steps for K factors or 2^K factors. Therefore, the number of possible combinations, N for K factors is $N=2^K=2^3=8$. The interest has been focused on the effect of three factors on the product yield (Y), viz. 100 to 300 % excess of ammonium nitrate, 25% less to 25% excess Decanol and reaction temperature in the rang of 800-1000 ^{0}C in argon atmosphere. The following relations have been considered

Mean, $Z_i^0 = (Z_i^{max} + Z_i^{min})/2$

$\Delta Zi = (Zi^{max} - Zi^{min})/2$

The point with coordinates (Z_1, Z_2, Z_3) are called the "Centre points of design" or "basic level." ΔZi is the "Change interval." It is useful to pass from Z_1, Z_2, Z_3 to a new dimension system X_1, X_2, X_3 by cooling equation:

$Xj = (Z_j - Z_j^0)/\Delta Z_j$, for j= 1,2,3

TABLE 1 shows the variable process parameters and their selected range. The design matrix and the results obtained from XRD peak height are shown in TABLE 2.

TABLE 2: The design matrix and the results obtained from XRD peak height

No.	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Peak height (cm)	Yi
SN-1	+1	+1	+1	+1	+1	+1	+1	+1	1.25	Y_1
SN-2	+1	+1	-1	+1	-1	+1	-1	-1	1.10	Y_2
SN-3	+1	-1	+1	+1	-1	-1	+1	-1	1.40	Y_3
SN-4	+1	-1	-1	+1	+1	-1	-1	+1	1.45	Y_4
SN-5	+1	+1	+1	-1	+1	-1	-1	-1	1.15	Y_5
SN-6	+1	+1	-1	-1	-1	-1	+1	+1	1.20	Y_6
SN-7	+1	-1	+1	-1	-1	+1	-1	+1	1.25	Y_7
SN-8	+1	-1	-1	-1	+1	+1	+1	-1	1.15	Y_8

The Regression equation is presented by:

$Y = B_0X_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{23}X_2X_3 + B_{123}X_1X_2X_3$

In the given equation the co-efficient B_0 represent the Si_3N_4 product obtained, when all the variables are at their base level. B_1, B_2 and B_3 represent the effect of individuals variables, B_{12}, B_{13}, B_{23} and B_{123} represent the effect of interaction of the variable. All B_j values have been calculated, considering the following equation and are shown in the TABLE 3:

$$Bj = 1/N \sum_{i=1}^{N} Xij \ Yi$$

The three replicate observation have been made at the centre point and mean of these is equal to$[Y^0]$

$$[Y^0] = \sum_{i=1}^{3} Yi0/3 = (125+120+125)/3$$

Then Se^2 and Sb_j values are calculated considering the given equations:

$$Se^2 = \sum_{i=1}^{3} (Yi - Y^0)^2 / 2 = 8.27 \times 10^{-4}$$

$$Sb_j = Se/N^{1/2} = 0.0103$$

The significance of the coefficients could be tested using students' test[14]. For a significance level of

TABLE 3: All Bj values are shown

B_0	1.243	B_{12}	0.0062
B_1	-0.069	B_{13}	-0.056
B_2	0.0189	B_{23}	-0.0156
B_3	0.056	B_{123}	0.0437

TABLE 4: All tj are shown

t_0	120.60	t_{12}	0.58
t_1	6.69	t_{13}	5.4
t_2	1.83	t_{23}	1.56
t_3	5.43	t_{123}	4.24

p=0.05 and degree of freedom f=2, the tabulated value of the Students't distribution is $t_p(f)=4.3$. All values have been calculated, considering the following equation and are shown in TABLE 4.

$$t_j = |\mathbf{Bj}| / \mathbf{Sb_j}$$

If t_j is less than t_p, then Bj is insignificant and hence discarded. Hence t_2, t_{12}, t_{23} and t_{123} are insignificant and significance terms l = 4. Hence, final regression is presented as:

$$\hat{Y} = 1.243 – 0.069\ X1 + 0.056\ X3 -0.056X1X3$$

Above estimated regression equation was tested to find how it fitted the observation using Fisher test, i.e variance ratio $F = Sr^2/Se^2$

$$Sr^2 = \{\sum_{i=1}^{8}(Yi-\hat{Y})^2\}N-1 = (4.78\times10^{-3})/4$$

$$F = 1.196\times10^{-3}/8.27\times10^{-4} = 14.4$$

The tabulated value of Fisher's F for p=0.05, $f_1=(N-l)=4$, $f_2= m-l=2$ is 19.92.

Since the computed value based on experimental result is 14.4, which is smaller than 19.92, therefore the above equation is statistically adequate. From the analysis of the design of experiments it may be inferred that

i. Synthesis of silicon nitride by in situ generation of nitrogen through sol-gel route is feasible.

ii. From the statistically adequate equation, it is found that coefficient of X_1 and X_3, i.e NH_4NO_3 and temperature variable is much greater than the other variable.

iii. Regression equation for the synthesis of silicon nitride by in situ generation of nitrogen through sol-gel route could be found out and they are statistically adequate within 95% confidence limits.

iv. Maximum recovery is obtained for all the design boundary surface corresponding to 100% excess NH_4NO_3 and 1000^0C temperature.

CONCLUSIONS

Nanosized Si_3N_4 was synthesized by in-situ generation of nitrogen through the sol-gel process. The crystallization of Si_3N_4 was observed at different temperatures. XRD and IR spectroscopy confirmed the synthesis of α- and β-Si_3N_4. The formation of Si_3N_4 by this in-situ generation of N_2, compared to the conventional process occurs at a comparatively lower temperature. From the above-described process, a simple and mild-condition synthesis of extremely fine nanosized Si_3N_4 in the range 6-2nm is proposed.

Regression equation for silicon nitride synthesis by in situ generation of nitrogen through sol-gel route could be found out and they are statistically adequate within 95% confidence limits.

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