

Synthesis of Si₃N₄ Powder by Carbothermic Reduction in Nitrogen

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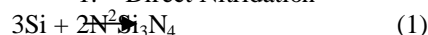
ABSTRACT: Silicon nitride can be accepted as one of the most important engineering ceramics for both today and in the future because of their excellent properties such as high temperature resistance, low density, high corrosion resistance and other mechanical properties. However, production methods of the silicon nitride are of both difficulties and high costly process. Five main methods to synthesis the silicon nitrides are used as mentioned in the previous studies. Carbothermal reduction and nitridation (CRN) process which is one of these methods is inexpensive and effective. In this study, Si₃N₄ powder was synthesized using carbothermic reduction and simultaneously nitriding method. For this study, starting material is quartz mineral, which was received from Ege-Sil Co., with carbon source as reducing agent. The powders were mixed and ball-milled, then were reacted in a tube furnace above 1400 °C for 4 hours flowing nitrogen gas. Powders were characterized using X-Ray Diffraction and Particle Size Distribution. The results were shown that production of α-Si₃N₄ were affected with some parameters related the process such as N₂ flow rate, conversion temperature, mixture rate and purity of the starting powder. The overall results revealed that the high quality powder can be obtained with the control and optimization of the process.

KEYWORDS: Si₃N₄, Conversion, CRN, Quartz.

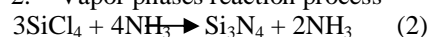
I. INTRODUCTION

Silicon nitride is an advanced compound, due to its excellent properties such as high hardness, good creep resistance, good oxidation resistance, thermal and chemical stability both room and high temperature. For these ceramics, biomaterials, turbochargers, cutting tools and engine parts can be said as some of used areas [1-5]. Silicon nitride can produce different methods such as carbothermal reduction and nitridation (CRN), direct nitridation, silicon diimide process, vapor phase reaction process and plasma synthesis [6-7].

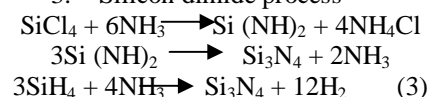
1. Direct Nitridation



2. Vapor phases reaction process



3. Silicon diimide process

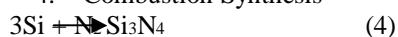


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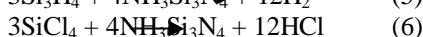
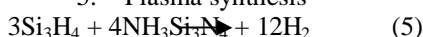
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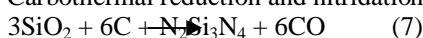
4. Combustion Synthesis



5. Plasma synthesis



6. Carbothermal reduction and nitridation



Each of the above reactions have some advantage and disadvantage. Process (1) is easily used to synthesis of reaction bonded silicon nitride from raw material. However, due to the reaction exothermic character, control of reaction is not easy. When synthesis of silicon nitride powder using processes (2) and (3), the product will be high quality with high surface area and fine particle size, but they are expensive methods. Combustion synthesis (CS) process (4) has great features such as energy efficiency, high production rate and high purity of powders. But, control of this method is quite difficult too [8-9]. Although the mechanism of the sintering process in plasma spray (5-6) is still unclear, a great number experimental study prove that rapid heating and relatively low sintering temperature are available and the total sintering time can be shortened. However, Plasma synthesis of Si_3N_4 is expensive [10-11].

One of the most used processes can be said carbothermal reduction and nitridation synthesis due both inexpensive and easier method. When the CRN process control is not achieved sensitively, produced silicon nitride has impurities, high oxygen low yield and agglomerated to a high degree. The carbothermal reduction and nitridation process is affected some parameters such as purity of starting powders, reaction temperature, milling time and nitrogen pressure. Starting materials play crucial role that reaction kinetics, thermodynamics and mechanism of CRN method. So that physical and chemical state of the starting materials, homogeneity of mixtures and specific surface area have vital effect on the CRN method [2]. It is shown previous studies that a significant influence between nitrogen pressure and heating rate on producing Si_3N_4 powders. It is known that during synthesis of silicon nitride two different structures which are named $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ occur as depend temperature. It has been reported that the carbothermal reaction starts at 1400 C as Si_3N_4 and phase transformation from $\alpha\text{-Si}_3\text{N}_4$ to $\beta\text{-Si}_3\text{N}_4$ occurs at temperature higher than 1600 C [12-16].

The goal of this study was to synthesis of Si_3N_4 powders by carbothermal reduction and nitridation process. Some process parameters was changed to optimise for CRN synthesis. The overall results revealed that the high quality powder can be obtained with the control and optimization of the process.

II. EXPERIMENTAL PROCEDURE

For experimental study, starting material is quartz mineral, which was received from Ege Kimya Company (Turkey) that is given its properties in Table 1. the Mastersizer 2000 (Malvern Instruments, Worcs., UK) was used to get Particle size distribution of raw material. Carbon black is used as reducing agent that received from (Vulcan XC 72 from CABOT), 99.7 % purity having a specific surface area of $110 \text{ m}^2 \text{ g}^{-1}$.

Table 1. Properties of quartz mineral supplied by Ege Kimya A.S., Turkey

Main phase (wt%)	Impurity (wt%)	Metallic Fe (wt%)	Density g/cm^3
SiO_2 (min 98 %)	Max. 2 %	Max. 0.05	2.65

Quartz was mixed with carbon black just above the stoichiometric amount of oxygen content in the SiO_2 . In order to have a homogeneous mixture, constituents were mixed in ball milling for 1 h. The mixed powders that was into an aluminum oxide crucible was placed in the hot zone of tube furnace. The carbothermic reduction and simultaneously nitridation reactions were carried out using a tube furnace at 1450°C for 2-4h under the flow of nitrogen gas (99.999 %

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purity from The Linde Group, Turkey). Thermal procedure is given Figure 1. The products were heated in an air for 1 h at 900°C for residual carbon burning after CRN process. Characterization of powders was analyzed (Rigaku, D/MAX/2200/PC, Japan) using a Cu Ka radiation source ($k = 1.540456 \text{ \AA}$) and the phases identified using X'Pert High Score.

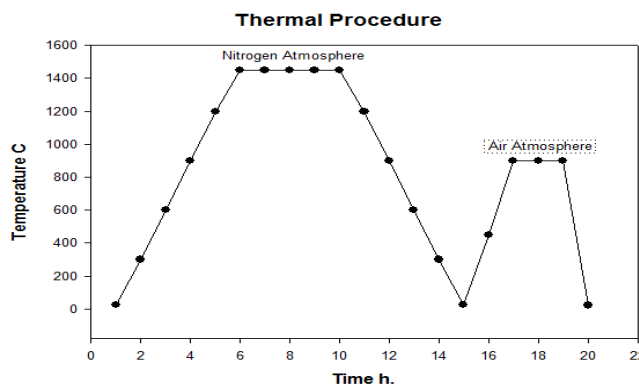


Figure 1. Thermal Procedure

III. RESULTS AND DISCUSSION

The particle size distribution (PSD), measured by laser diffractometry of SiO_2 as raw material are given in Fig. 2. The PSD shows that the particle size distribution has narrow and homogeneous distribution characteristics. Fig 2 shows that the SiO_2 powder has $d(0.1)$: 4.892 μm , $d(0.5)$: 13.490 μm and $d(0.9)$: 34.003 μm particle size value for the raw material. The calculated specific surface area (SSA) of the SiO_2 powder was 0.67 m^2/g . This means great surface area to react with carbon, and clearly fine powder.

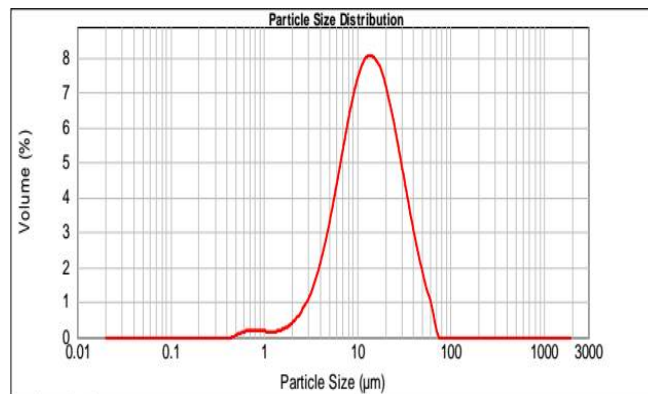


Figure 2. Particle size distribution of the raw material

After the conversion reactions, the first indicator to find out about conversion that is a change in color of the powder mixture from black to white tones. Final product in a khaki-colored powder was obtained by the burn-out of excess carbon. The color change after the CRN (still with excess carbon) can easily be shown in Fig. 4. The color change was reported by previous works [5, 18]. Stoichiometric ratio is very important parameters in this process. Because, addition of carbon into silica, providing that out of this ratio, can results in either formation of silicon carbide phase or residual unreacted silica [17, 18].

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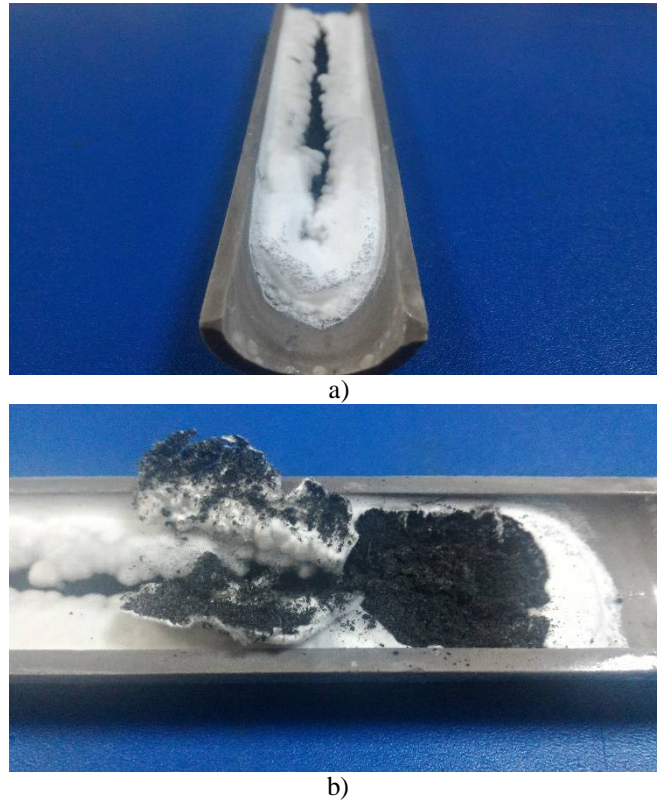


Figure 3. Colour of the product after the CRN

Color change of resulting powder can present practical pre knowledge about conversion but it is never supply phase content. For this aim, determination of phase content can be possible with analyzing by X-Ray Diffraction. The X-Ray diffractograms of the resulting powder obtained by carbothermal reduction and nitridation confirmed phase formation as illustrated in Figure 4. Peaks on the graphic revealed that dominant peaks belonged to silicon nitride phase. It is well known that silicon nitride has two types crystallography, alpha phase which is the low temperature form and beta phase which is the high temperature form. Fig. 4 shows that while alpha phase occurred as dominant phase, beta silicon nitride as minor phase was present as recessive phase. In addition, there was minor undefined phase.

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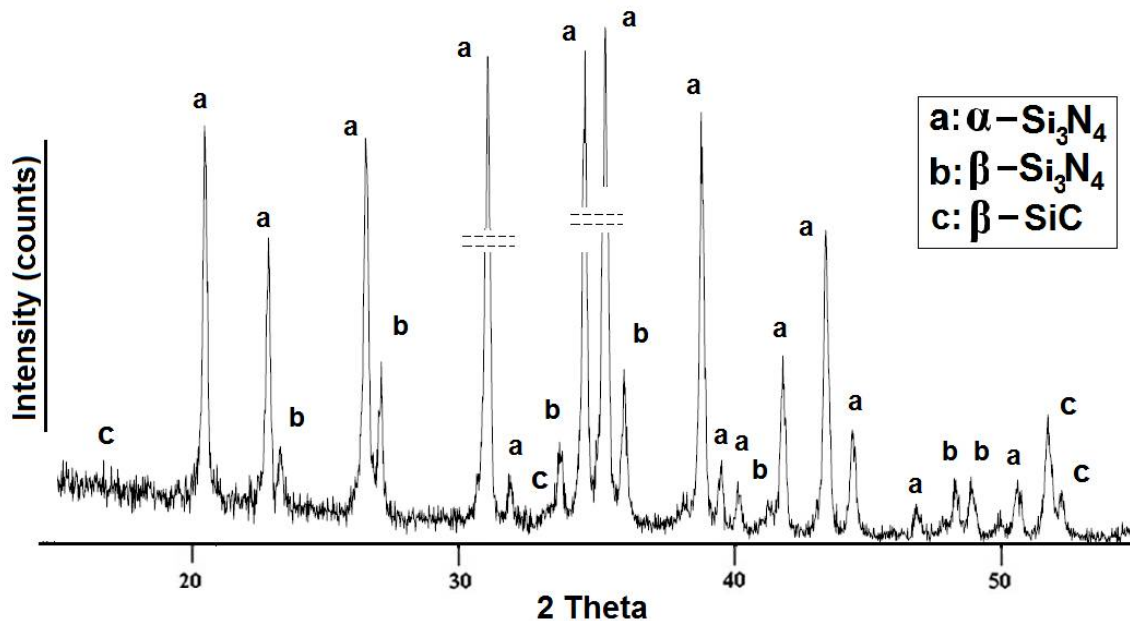


Figure 4. XRD patterns of the reacted SiO_2/C powders after the CRN.

IV. CONCLUSION

In this study, silica was reacted with carbon as a reducing agent at elevated temperature to achieve the synthesis of Si_3N_4 powders by carbothermal reduction and nitridation process. The CRN process came to the forefront to product inexpensive silicon nitride powder. To sum up, the results showed that synthesis of silicon nitride ceramic powder was substantially achieved with minor other phase. The authors can evaluate that the result Si_3N_4 powder can easily be used in various field such as chemical applications, wear systems, refractory components, etc. This process has a great improvement potential of synthesis of monophasic alpha or beta silicon nitride.

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