

Special Issue of the 6th International Congress & Exhibition (APMAS2016), Maslak, Istanbul, Turkey, June 1–3, 2016

# The Carbothermal Reduction of Silica with $Y_2O_3$ –MgO Powders

N. CANIKOĞLU\*

Sakarya University, Engineering Faculty, Department of Metallurgy and Materials Engineering,  
54187, Sakarya, Turkey

The aim of this study is to examine the effect of MgO and  $Y_2O_3$  to the carbothermal reduction and nitridation of silica. The synthetic silica, MgO and  $Y_2O_3$  powders were premixed (4wt% MgO–6%  $Y_2O_3$ , 5% MgO–5%  $Y_2O_3$  and 6% MgO–4%  $Y_2O_3$ ) in the starting reactants depending on the final powder composition. Carbon black was added to the silica ( $SiO_2$ ) above the stoichiometric amount of oxygen (C/ $SiO_2$  ratio of 3). The carbothermal reduction and nitridation process was carried out in a tube furnace at 1400 °C, 1450 °C, and 1475 °C for 3 h under nitrogen gas atmosphere. The synthesized  $Si_3N_4$  powder properties were examined by using X-ray diffraction, scanning electron microscopy–energy dispersive X-ray spectroscopy. In this study, MgO and  $Y_2O_3$  powders dispersed in the final  $Si_3N_4$  powder more homogeneously and thus formable and sinterable the starting mixing material is produced.

DOI: [10.12693/APhysPolA.131.162](https://doi.org/10.12693/APhysPolA.131.162)

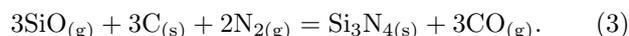
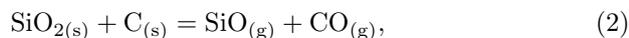
PACS/topics: 81.05.Je

## 1. Introduction

Silicon nitride ceramics of superior properties such as high hardness, high temperature strength, excellent thermal shock resistance, oxidation-proof and chemical corrosion-proof have been widely used in the field of energy, metallurgy, machinery, and aerospace industries [1, 2]. These materials are used heavily in cutting tools, ball bearings, motor valves, and the other wear resistant tools [3]. Techniques applied to fabricate silicon nitride include: direct nitridation of silicon, high-temperature decomposition of silicon diimide, SiO vapor ammonolysis, and carbothermal reduction and simultaneous nitridation (CRN) of silica. Amongst these methods, the CRN route is one of the most cost effective routes for industrial production [4]. The carbothermal reduction takes place according to the following overall reaction [5]:



It is generally accepted in the literature that this reaction occurs through the formation of an intermediate SiO vapour phase, according to the following reactions [6, 7]:



Moreover, the competitive formation of silicon carbide has been reported at temperatures higher than 1500 °C.  $Si_3N_4$  occurs in two phases  $\alpha$  and  $\beta$ . The  $\alpha$  phase powder is the generally preferred raw material for manufacturing compacted bodies because of the favourable microstructural characteristics obtained during the  $\beta$  transformation at high temperatures [5].

$Si_3N_4$  ceramics are prepared by liquid phase sintering: at typical temperatures  $\geq 1700$  °C, sintering additives form a melt, which dissolves the  $\alpha$ - $Si_3N_4$  crystallites.  $\beta$ - $Si_3N_4$  nuclei grow by reprecipitation [8]. Generally, metal oxides, such as MgO,  $Al_2O_3$ ,  $Y_2O_3$ ,  $Yb_2O_3$ ,  $La_2O_3$ , and  $Lu_2O_3$ , were used as sintering additives [9–11], which can react with  $Si_3N_4$  and  $SiO_2$  on the surface of  $Si_3N_4$  powder at a high temperature to form M–Si–O–N liquid phase. Besides of oxide additives, nitrides, such as AlN, YN, TaN,  $Mg_3N_2$  and  $Be_3N_2$  have also been adopted as additives to manufacture silicon nitride ceramics [12].

The aim of this study is to synthesize and characterize of silicon nitride containing  $Y_2O_3$  and MgO. Consequently, silicon nitride is produced by the carbothermal reduction and nitridation of silica at a low temperature with these additives.

## 2. Experimental procedure

For the CRN of silica ( $SiO_2$ ), high purity (99%) silica of nearly colloidal range (14  $\mu$ m) was used to as raw material and it was supplied from EGE Kimya A.S. Activated charcoal (100% purity) was used as a reducing agent and it was supplied by TÜPRAŞ (Turkish Petroleum Refineries Co). MgO and  $Y_2O_3$  powders (99.9% purity) were supplied by Alfa Aesar. Carbon black was added to the high purity  $SiO_2$  above the stoichiometric amount of oxygen (C/ $SiO_2$  ratio of 3). MgO and  $Y_2O_3$  powders were added at different rates depending on the final powder composition (Table I). Dry mixing was performed by ball milling for 10 h with alumina balls for all compositions. The differential thermal analysis–thermogravimetric (DTA-TG) analysis was applied to the one of the prepared mixtures ( $SiO_2$ 5MgO–5 $Y_2O_3$ –C). Later, the carbothermal reduction of silica was carried out in an atmosphere controlled tube furnace. For all compositions, the synthesis was performed under the nitrogen gas flow (1 l/m) at 1400 °C, 1450 °C, and 1475 °C for 3 h. After

\*e-mail: [nurayc@sakarya.edu.tr](mailto:nurayc@sakarya.edu.tr)

the CRN process, the powder products were heated in air for 1 h at 900 °C for residual carbon burning. Table I gives the identification code for each powder with its production conditions in the CRN process.

TABLE I

The codes and production parameters for powders.

Composition	Sample code
SiO <sub>2</sub> +%4MgO-%6Y <sub>2</sub> O <sub>3</sub>	4MY
SiO <sub>2</sub> +%5MgO-%5Y <sub>2</sub> O <sub>3</sub>	5MY
SiO <sub>2</sub> +%6MgO-%4Y <sub>2</sub> O <sub>3</sub>	6MY

A DTA was carried out using a differential thermal analyser (TA Instrument Q-600). X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and Cu K<sub>α</sub> radiation. A JEOL 6060 LV scanning electron microscope with EDS was used for microstructural analysis.

### 3. Results and discussion

For the SiO<sub>2</sub>+%5MgO+%5Y<sub>2</sub>O<sub>3</sub>+C mixture was carried out the DTA-TG test under N<sub>2</sub> gas atmosphere to determine the temperatures of the reduction and nitriding reactions and obtained graph was given in Fig. 1. In the around 200 °C the weight loss was observed due to absorbed moisture in the TG curve. The onset temperature for the second weight loss was 450 °C approximately due to the reduction of SiO<sub>2</sub>. The nitridation stage was seen after reduction of SiO<sub>2</sub> around 1300 °C. In a previous work [13], the reduction and nitridation temperatures of SiO<sub>2</sub> were determined from the DTA analyses as 850 °C and 1400 °C, respectively. These temperatures were decreased with the presence together of MgO and Y<sub>2</sub>O<sub>3</sub>.

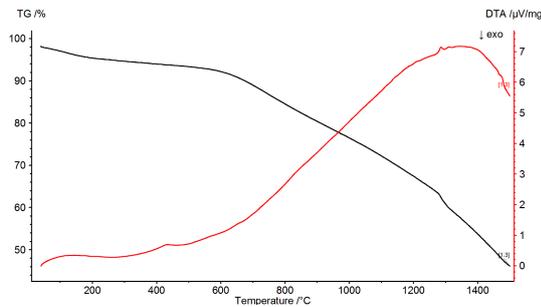


Fig. 1. The DTA-TG curves of SiO<sub>2</sub> + %5MgO + %5Y<sub>2</sub>O<sub>3</sub> + C mixture.

In Fig. 2a-c the XRD analyses were given of the produced samples with the CRN process. Given in Fig. 2a in the sample 4MY, α-Si<sub>3</sub>N<sub>4</sub> was obtained at 1400 °C for 3 h, in addition Mg<sub>2</sub>SiO<sub>4</sub> and Y<sub>2</sub>SiO<sub>5</sub> phases occurred in a small amount. The formation of an amorphous phase was observed at 1450 °C. This formation disappeared with increase of temperature to 1475 °C and β-Si<sub>3</sub>N<sub>4</sub> amount was increased. This was caused decrease of the intensities of α phase. As seen from the XRD analyses of samples

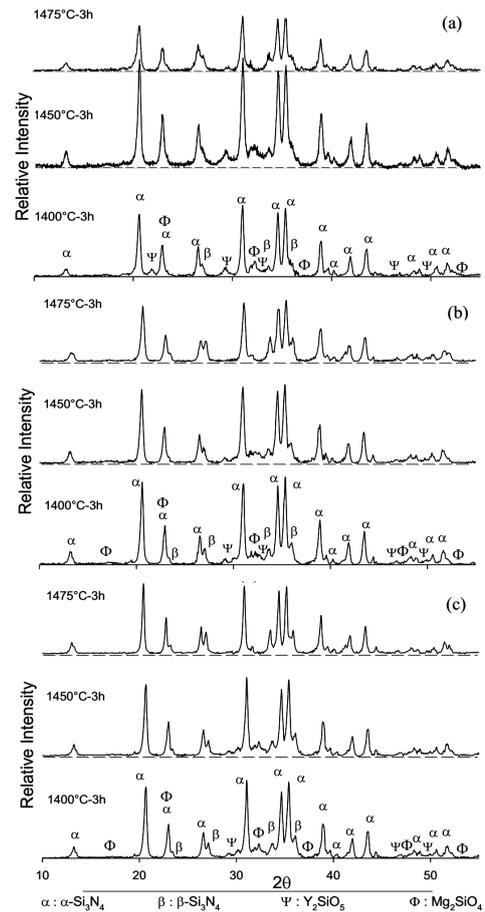


Fig. 2. The XRD analysis of samples: (a) 4MY, (b) 5MY, (c) 6MY after CRN process.

5MY (Fig. 2b), the CRN took place at 1400 °C. The produced powder at 1400 °C was fully converted to α and β-Si<sub>3</sub>N<sub>4</sub>, and a minor amount of Y<sub>2</sub>SiO<sub>5</sub> and Mg<sub>2</sub>SiO<sub>4</sub> (forsterite) phases as expected were present. The composition and contents of the sintering aids strongly affect the microstructure and mechanical properties of silicon nitride ceramics. Metallic oxides (e.g., MgO, Y<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>) or rare earth metal oxides (e.g., La<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub>) are frequently used as sintering aids [14].

Mg<sub>2</sub>SiO<sub>4</sub> shows good refractoriness due to high melting point (≈ 1890 °C), low thermal expansion, good chemical stability, and excellent insulation properties even at high temperatures [15]. As an important phase in the SiO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-Si<sub>3</sub>N<sub>4</sub> phase diagram, Y<sub>2</sub>SiO<sub>5</sub> is frequently identified as a precipitated phase at the grain boundaries of sintered Si<sub>3</sub>N<sub>4</sub> with Y<sub>2</sub>O<sub>3</sub> or Y<sub>2</sub>O<sub>3</sub>+ SiO<sub>2</sub> as sintering aids. It was confirmed that Y<sub>2</sub>SiO<sub>5</sub> can improve the high-temperature performance of silicon nitride [16, 17]. It was thought that the presence of these phases in the powders as-synthesized can improve the high temperature properties after the sintering of the powders. Figure 2c gives the XRD analyses of samples 6MY. As clearly seen from the XRD data, α - β Si<sub>3</sub>N<sub>4</sub>, Y<sub>2</sub>SiO<sub>5</sub> and Mg<sub>2</sub>SiO<sub>4</sub> phases were formed in sample 6MY as sample 5MY at 1400-

1450–1475 °C for 3 h after the carbothermal reduction and nitridation process. It is known that  $\alpha$ - $\text{Si}_3\text{N}_4$  starting powders have a higher reactivity and are used more widely than  $\beta$ - $\text{Si}_3\text{N}_4$  powder. When  $\beta$ - $\text{Si}_3\text{N}_4$  powder is used as starting powder, the formation and densification of the elongated  $\beta$ - $\text{Si}_3\text{N}_4$  grain are rather difficult [18]. Consequently, there was a high amount of  $\alpha$ - $\text{Si}_3\text{N}_4$  and a low amount of  $\beta$ - $\text{Si}_3\text{N}_4$  in the produced powders in this study.

The morphology, structure and elemental analysis of the as-synthesized powder have been characterized with SEM and EDS techniques. The SEM micrographs of the produced powders are shown in Fig. 3. It is clearly seen that powder products have different morphologies, as nanosized whiskers, irregular shaped small particles, and equiaxed small grains. The typical widths of the whiskers are in the range of 100–500 nm, also small particles are nanosized, too. With increased  $\text{Y}_2\text{O}_3$  amount the whisker structure was increased (Fig. 3e–f).  $\text{MgO}$ - $\text{Y}_2\text{O}_3$  was added into  $\text{SiO}_2$  by CRN process in this technique, therefore the nanosized  $\alpha$ -rich  $\text{Si}_3\text{N}_4$  is produced with a homogeneous additives distribution in the structure at low temperature (1400 °C–3 h). Adding a rare earth alone (< 10 wt%) is not as effective as sintering aid concurrent additions of rare earth and metal oxides are usually done to increase the sinterability [19]. When the synthesizing conditions (amount and type of additives and temperature) are compared with the previous works [12, 13, 20], it is seen that these conditions are better.

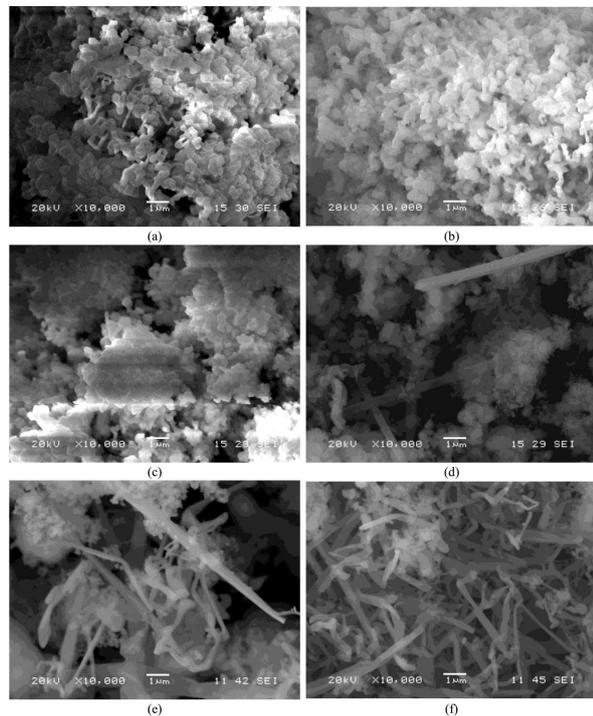


Fig. 3. The SEM analyses of sample: (a) 4MY at 1400 °C, (b) 4MY at 1475 °C, (c) 5MY at 1400 °C, (d) 5MY at 1475 °C, (e) 6MY at 1400 °C and (f) 6MY at 1475 °C after CRN process.

#### 4. Conclusions

In this work,  $\text{Si}_3\text{N}_4$  powders were synthesized by carbothermal reduction and nitridation process from high purity  $\text{SiO}_2$  with  $\text{Y}_2\text{O}_3$ - $\text{MgO}$  additives. Here, the effect of composition and temperature was investigated. According to the analysis results, the optimum conditions were determined as %5 $\text{MgO}$ +%5 $\text{Y}_2\text{O}_3$ + $\text{SiO}_2$  mixture and 1400 °C. The grain size and whiskers' widths of the powders produced under these conditions are submicron and in the range of 100–500 nm, respectively. The positive effects of using  $\text{Y}_2\text{O}_3$ - $\text{MgO}$  as pre-additive oxides in  $\text{SiO}_2$  on the yield of  $\text{Si}_3\text{N}_4$  in CRN process were clear from the outcomes of this research in terms of reaction temperature and time.

#### References

- [1] Y. Li, L. Wang, S. Yin, F. Yang, *Mater. Chem. Phys.* **141**, 874 (2013).
- [2] L. Zhoua, Y. Huang, Z. Xie, A. Zimmermann, F. Aldinger, *J. Europ. Ceram. Soc.* **22**, 1347 (2002).
- [3] R. Shuba, Ph.D. Thesis, Pennsylvania University, 2005.
- [4] H. Ji, Z. Huang, K. Chen, W. Li, Y. Gao, M. Fang, Y. Liu, X. Wu, *Powder Technology* **252**, 51 (2014).
- [5] A. Ortega, M.D. Alcala, C. Real, *J. Mater. Process. Technol.* **195**, 224 (2008).
- [6] F.L. Silva, J.M. Vieira, *J. Mater. Process. Technol.* **92-93**, 112 (1999).
- [7] H. Arik, *J. Europ. Ceram. Soc.* **23**, 2005 (2003).
- [8] E. Kroke, M. Schwarz, *Coord. Chem. Rev.* **248**, 493 (2004).
- [9] A. Vuckovic, S. Boskovic, B. Matovic, M. Vljajic, V. Krstic, *Ceram. Int.* **32**, 303 (2006).
- [10] X. Zhu, Y. Sakka, Y. Zhou, K. Hirao, *Acta Mater.* **55**, 5581 (2007).
- [11] S. Fünfschilling, T. Fett, M.J. Hoffmann, R. Oberacker, T. Schwind, J. Wippler, T. Böhlke, H. Özcbaban, G.A. Schneider, P.F. Becher, J.J. Kruzic, *Acta Mater.* **59**, 3978 (2011).
- [12] Z.H. Liang, J. Li, L.C. Gui, G.H. Peng, Z. Zhang, G.J. Jiang, *Ceram. Int.* **39**, 3817 (2013).
- [13] N. Karakuş, A.O. Kurt, H.Ö. Toplan, *Ceram. Int.* **35**, 2381 (2009).
- [14] H.H. Lu, C.Y. Chen, *Ceram. Int.* **42**, 12452 (2016).
- [15] A. Saberi, B. Alinejad, Z. Negahdari, F. Kazemi, A. Almasi, *Mater. Res. Bull.* **42**, 666 (2007).
- [16] Z. Sun, M. Li, Y. Zhou, *J. Europ. Ceram. Soc.* **29**, 551 (2009).
- [17] D. Li, M. Li, *J. Mater. Sci. Technol.* **28**, 799 (2012).
- [18] K. Chen, Z. Huang, Y.G. Liu, M. Fang, J. Huang, Y. Xu, *Powder Technol.* **235**, 728 (2013).
- [19] X.J. Liu, Z.Y. Huang, Q.M. Ge, X.W. Sun, L.P. Huang, *J. Europ. Ceram. Soc.* **25**, 3353 (2005).
- [20] N. Karakuş, A.O. Kurt, H.Ö. Toplan, *Mater. Manufact. Process.* **27**, 797 (2012).