Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 2381–2385
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Synthesizing high α-phase Si_3N_4 powders containing sintering additives

Nuray Karakuş *, A. Osman Kurt, H. Özkan Toplan

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

Received 20 August 2008; received in revised form 8 September 2008; accepted 2 February 2009
Available online 25 February 2009

Abstract

Fine grain α-phase silicon nitride (Si_3N_4) ceramic powders were produced via carbothermic reduction of colloidal SiO_2, which contained pre-mixed additives of sintering aids primarily consisting of oxides such as MgO and Y_2O_3. The powders that were pre-mixed in the starting reactants were chosen based on the final powder composition and on type and amount of the secondary phases desired for sintering. After synthesizing, powder properties were examined using standard characterization techniques (XRD, SEM, BET, etc). This technique of ceramic synthesis has advantages in providing nitride-based ceramic powders, which contain secondary in situ phases that are distributed as sintering additives. Silicon nitride ceramic powders synthesized using this method might therefore be readily sintered because the homogeneously distributed sintering additives were present in the starting materials. In this work, the processing parameters are described in terms of the synthesis conditions.

Keywords: Silicon nitride; Powder; Synthesis; Microstructure

1. Introduction

Structural ceramics based on silicon nitride (Si_3N_4) and related compounds have been extensively researched for more than three decades. They exhibit excellent mechanical properties, good oxidation resistance and a thermal shock behavior at both room and high temperatures [1]. In recent years, silicon nitride ceramics have been used in the structural components of gas turbines, engines and other structures subjected to high-temperature conditions [2]. Silicon nitride ceramics, like other nitrides, must be produced synthetically. There are several different production routes for Si_3N_4 powders. These methods include direct nitridation of silicon, carbothermic reduction of silica, diimide synthesis, vapor phase synthesis, plasma chemical synthesis, pyrolysis of silicon organic compounds and laser-induced reactions. The most popular techniques are the direct reaction between silicon (Si) and nitrogen (N_2) (Eq. (1)), and the carbothermal reduction of silica (SiO_2) (Eq. (2)) using reducing agents (mainly carbon) in nitrogen [3,4].

Nitridation of metallic silicon powder:

$$3Si_{(s)} + 2N_{2(g)} \overset{(1200-1500\,^{\circ}C)}{\longrightarrow} Si_3N_{4(s)} \quad (1)$$

Carbothermal reduction of SiO_2 in nitrogen:

$$3SiO_2 + 6C_{(s)} + 2N_{2(g)} \overset{(1200-1700\,^{\circ}C)}{\longrightarrow} Si_3N_{4(s)} + 6CO_{(g)} \quad (2)$$

Here, the final composition of the reaction products could be influenced by the following factors: the C/SiO_2 ratio and the textural characteristics of the starting materials (i.e., grain size, particle size distribution and grain morphology), the reaction gas composition and the synthesis temperature. Various authors have studied the influence of the experimental parameters on the synthesizing conditions of the final products after Reactions (1) and (2) [5].

Due to its highly covalent bonding character, Si_3N_4 and its derivatives (i.e., SiAlONs) cannot be densified using solid-state sintering techniques. In order to obtain high-density bodies, sintering aids have to be added to the starting powders [6–8]. Sintering aids such as metal oxides and rare earth metal oxides are used to promote densification through liquid-phase sintering. During sintering, the oxide additives react with silica (SiO_2) on the surface of Si_3N_4 particles to form a vitreous flux at the sintering temperature thereby assisting mass transport during densification [9]. Sintering aids such as

* Corresponding author. Tel.: +90 264 2955763; fax: +90 264 2955549.
E-mail addresses: nurayc@sakarya.edu.tr, cnuray@gmail.com (N. Karakuş).

0272-8842/$34.00
doi:10.1016/j.ceramint.2009.02.002

MgO, Y_2O_3 and Al_2O_3 added in α-Si_3N_4 powders, must be homogeneously distributed and possess the desired powder composition before shaping and sintering [10]. Distribution is usually performed by using an oxygen-free aqueous medium. Therefore, having a sinterable Si_3N_4 starting powder lowers production costs. Consequently, lowering production costs is the impetus behind the current study.

2. Experimental methods

In the present work, fine grain α-phase Si_3N_4 ceramic powders containing a desirable amount of sintering additives were synthesized using a carbothermal reduction–nitridation (CRN) technique. The starting agent for silicon source was high-purity (99%) synthetic silica of nearly colloidal range with a mean particle size of 14 μm and specific surface area of 139 $m^2\ g^{-1}$ (BET). Silica containing small amounts of Na_2SO_4 was supplied from EGE Kimya A.Ş. Activated charcoal of 98.4% purity with a mean particle size of 30 μm was supplied by Merck and was used as a reducing agent. MgO and Y_2O_3 were 99.9% pure, and were supplied by Alfa Aesar.

Carbon was added to the high-purity SiO_2 above the stoichiometric amount of oxygen. MgO and Y_2O_3 were premixed in the starting reactants depending on the final powder composition and the type and amount of the secondary phases desired for sintering. Mixing was performed by ball milling for 10 h with alumina balls.

The synthesis was carried out in a tube furnace at different temperature ranges under the various flow rates of nitrogen gas (99.99% pure). Nitrogen flow to the reaction tube was set up in a stepwise manner so that a minimum level of gas consumption could be achieved after following the DTA data of the SiO_2–MgO–carbon mixture. After the furnace was charged, it was vacuumed before backfilling with N_2. The N_2-flow rate was maintained at 1 l/min for 15 min and then lowered to 0.4 l/min and maintained at this rate until the furnace reached 900 °C. From 900 °C to a plateau temperature, gas flow rate was reset to 1 l/min. After holding at a plateau temperature at a predetermined time, the furnace was allowed to cool to room temperature. Gas flow was stopped for cooling when the temperature decreased to 900 °C. After the CRN process, the products were heated in air for 1 h at 900 °C for residual carbon burning.

The identification of the crystalline phases in the final product powders was carried out by X-ray diffraction (XRD) with Cu Kα (λ: 1.54056) radiation using a RIGAGU D/Max 2200 diffractometer. The particle size and morphology of the final products obtained after CRN were characterized using SEM (JEOL JSM-6060 LV) attached to an energy dispersive spectrometer (EDS). The EDS was also used to determine the elemental composition of the synthesized ceramic particles.

Previously, one of the authors used a type of magnesium silicate as a natural starting material for the synthesis of Si_3N_4 powders using the CRN process [11]. In that previous work, it was reported [11] that Mg present initially in the system had facilitated the formation of Si_3N_4 when compared to using a pure silica system [4]. Consequently, in the current work, unmodified high-purity synthetic SiO_2 admixed with 5% MgO was used in order to see the effect of MgO addition on the formation of Si_3N_4 powders after the CRN process. Readily sinterable α-phase Si_3N_4 ceramic powders were formed from using these additives. It is not within the scope of this paper to present results concerning the sintering behavior and performance of the product powders obtained from the CRN process. Instead, the CRN process will be presented as a flexible method that could be adjusted to obtain silicon nitride-based ceramic powders with desired specifications suitable for sintering. The first outcomes from the sintering test of as-synthesized powders are promising, but experiments must be repeated to guarantee reproducibility of this technique.

3. Results and discussion

Firstly, a DTA–TG test was carried out under N_2-atmosphere for the $SiO_2 + MgO + C$ mixture to determine the onset temperatures for the reduction and nitriding reactions (Fig. 1). The first endothermic peak below 200 °C was attributed with the weight loss due to absorb moisture. The onset temperature for the second weight loss was around 850 °C due to the reduction of SiO_2. From this temperature until 1400 °C the weight loss was steadily continued to reduce before finally level off. Simultaneous reduction of SiO_2 (and SiO) and nitridation of Si take place after 1400 °C (Fig. 1).

The addition of MgO and charcoal into the mixture of SiO_2 had an important effect on the CRN process for the synthesis of Si_3N_4 powders by lowering the process temperature and time. This result is shown in Fig. 2, where only the temperature range between 1375 and 1475 °C is given. Although reaction temperatures above and below these values were examined, results in the most significant range (i.e., 1375–1475 °C) are reported in this work. During the three-hour reaction, rates of heating (5 °C/dk), cooling (5 °C/dk) and N_2 flow were kept constant.

Fig. 2 clearly reveals that significant amounts of α-Si_3N_4 were formed at a temperature of 1375 °C after 3 h of reaction. In addition, large amounts of the intermediate phase (silicon oxinitride, Si_2N_2O) found in the product powders indicates that holding time and/or temperature constant was not enough to complete the reaction. The appearance of enstetite occurred at 1375 and 1400 °C, respectively. Enstetite and forsterite phases were expected since pre-additive MgO could easily be reacted with SiO_2 to form these low and high-temperature silicate phases. Among these intermediate phases, only forsterite remained when the temperature increased from 1450 to 1475 °C. At these temperatures (1450–1475 °C), Si_2N_2O and enstetite are disappearing to form Si_3N_4 and forsterite, respectively. Consequently, the optimum temperature for the formation of α-phase Si_3N_4 was found to be 1450 °C, above which the β/α ratio increases and forsterite starts to reduce (Fig. 2). This behavior is possibly a result of Mg heat reduction through either an elemental form or an unstable oxide compound, which may result in the formation of Si_3N_4 in the β-phase.

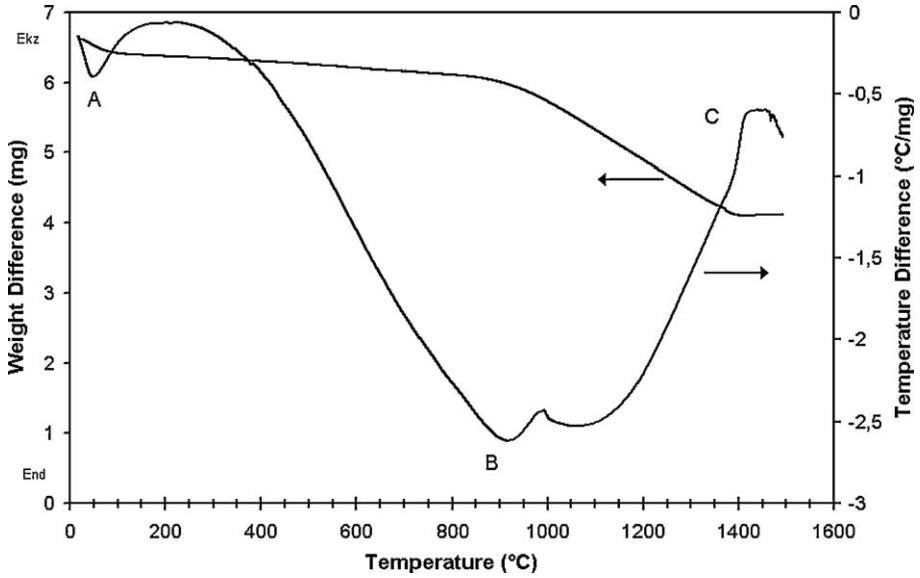

Fig. 1. The DTA–TG curves of SiO_2 + MgO + C mixture in nitrogen atmosphere.

The positive effects of MgO pre-addition to the reaction mixtures during CRN were obvious in two ways. First, the addition lowered the reaction temperature by a factor of 50 °C. Second, the holding time was reduced by 20–25% (3 h) compared to 1500 °C and 4–5 h reported in similar studies carried out previously [4,12]. In our system, having no such additives, the temperature of 1475 °C and the reaction duration of 6 h were required in order to achieve same results (Fig. 3). However, below this temperature or time, it was not possible to fully complete the reaction to form α-phase Si_3N_4 without pre-additives of oxides before CRN (Fig. 3).

Because of the positive effects of MgO addition on the Si_3N_4 yield, the same process was applied to the as-received SiO_2–charcoal mixture using Y_2O_3 as a pre-additive oxide (5 wt.%). Keeping all other parameters constant, the best results using Y_2O_3 admixed SiO_2 for a high α-phase yield was obtained at 1475 °C after a 3 h reaction (Fig. 4). The optimum temperature for the formation of α-Si_3N_4 using Y_2O_3 was 25 °C higher than for the product powders that used MgO. The results were promising in terms of the product phases and of the amount of β-Si_3N_4 found in the α-form powders (Fig. 2), where the synthesized product powder was compared to the commercial one. The reaction material was fully converted to α-Si_3N_4, although a small amount of β-phase along with a minor amount of $Y_5Si_3O_{12}N$ phase was present. This phase is desirable as aids for later stage of sintering.

The positive effects of using pre-additive oxides in SiO_2 on the yield of Si_3N_4 were clear. Y_2O_3 or MgO must have reacted with the silica at an early stage of the CRN process to form intermediate silicate phases. This action might have helped to

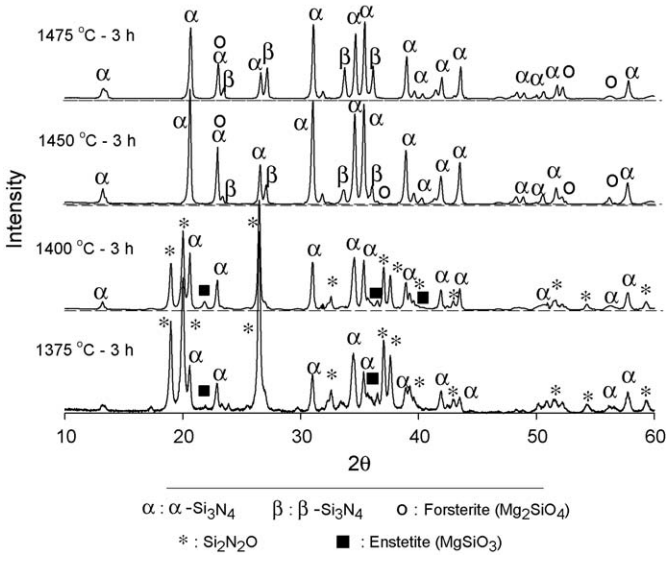

Fig. 2. Phases formed at different temperatures (1375–1475 °C) after CRN of the SiO_2 mixture, 5 wt.% MgO and carbon. Holding time and N_2 flow rate were kept constant for 3 h and at 1 l/min, respectively.

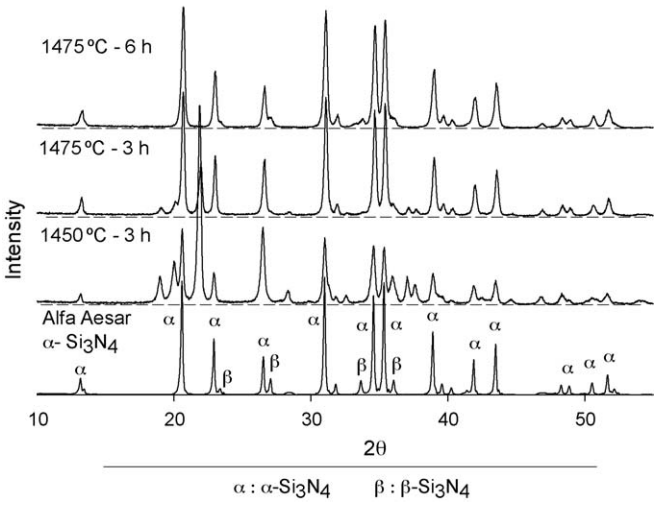

Fig. 3. XRD analysis of the product powders without pre-additives of oxides. The first sample is from Alfa Aesar used for comparison.

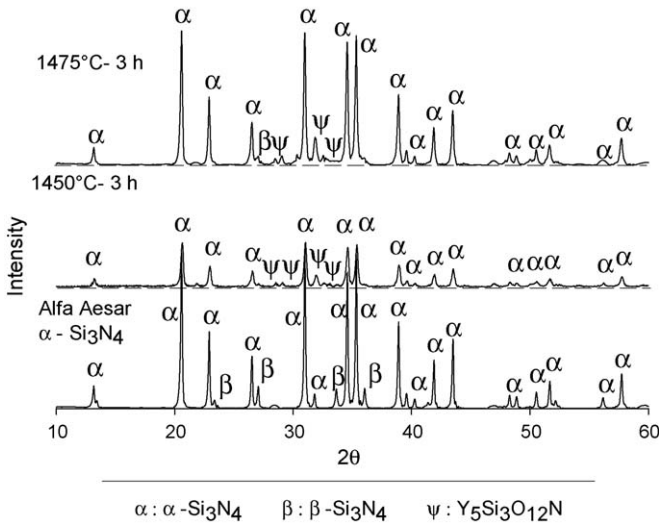

Fig. 4. Si_3N_4 powders produced at 1450 and 1475 °C for 3 h using SiO_2–5% Y_2O_3. The first sample is from Alfa Aesar (α-Si_3N_4, 6.39 $m^2\ g^{-1}$) used for comparison.

lower the stability of the system, which may have resulted in an increase in the formation of the sub-micron sized Si_3N_4 grains (Figs. 5–7).

SEM revealed that the powders obtained after CRN processes using MgO and Y_2O_3 admixtures in the starting material were very small in size and posed surface areas of 4.73 and 3.9 $m^2\ g^{-1}$, respectively (Figs. 5–8). The surface measured with the BET technique supported these results. Two major morphologies exist. One morphology possesses very long whiskered grain having submicron sized cross section (actually less than 200 nm), while others had very small, equiaxed grains agglomerated in a few micrometers (Figs. 5 and 7). Typical EDS patterns only showed that Si and N were present in the fibers and that Si, Mg, O and N were present in equiaxed grains (validation of the Mg_2SiO_4 phase) (Figs. 6 and 8).

SEM micrographs of the product powder synthesized from SiO_2–5% Y_2O_3 at 1475 °C for 3 h revealed different morphologies ranging from irregular shaped small particles to equiaxed small grains and long whiskers (Figs. 7 and 8). The long whiskers had a cross-section of approximately less than

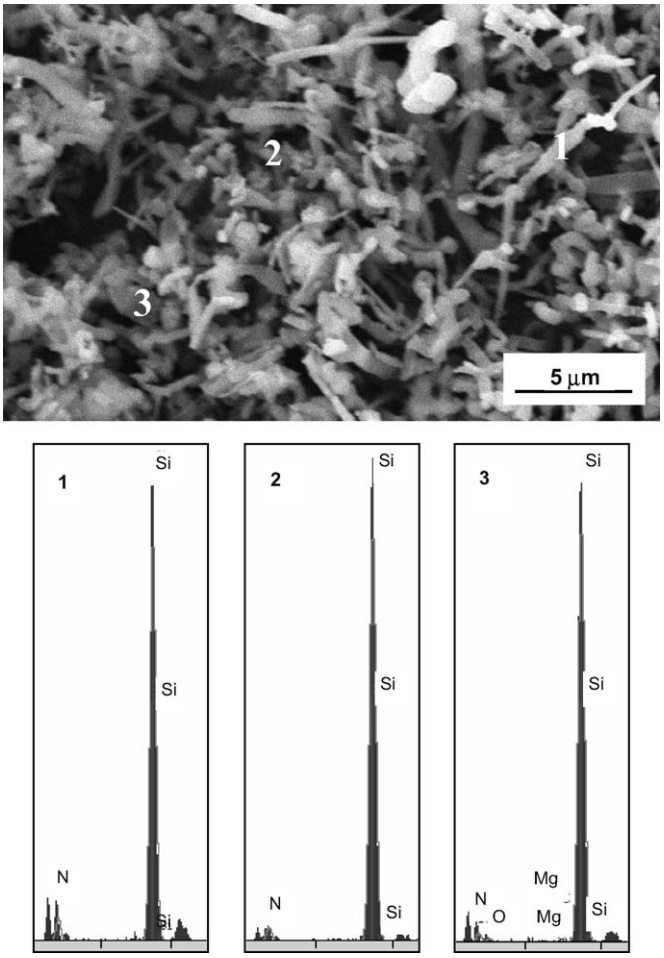

Fig. 6. EDS pattern of the powders synthesized from SiO_2–5% MgO at 1450 °C for 3 h.

500 nm. EDS patterns given in Fig. 6 showed that Si, Y, O and N elements could be detected from the small particles. Because of the very small, bi-modal grain morphology of the powders, it was difficult to detect the individual Si_3N_4, $Y_5Si_3O_{12}N$ particles. EDS could not detect sodium that was initially present in the SiO_2. Sodium might have already been driven off during the high-temperature reaction.

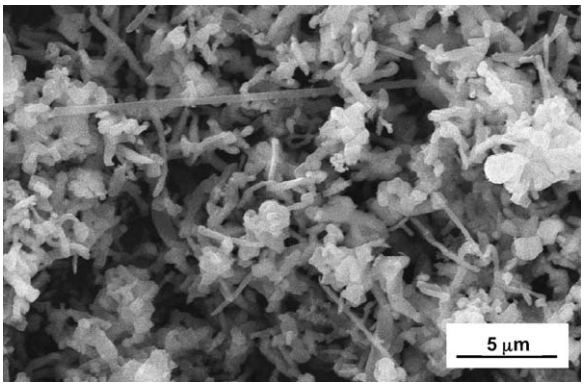

Fig. 5. SEM micrographs of the product powder (4.73 $m^2\ g^{-1}$) synthesized from SiO_2–5% MgO at 1450 °C for 3 h.

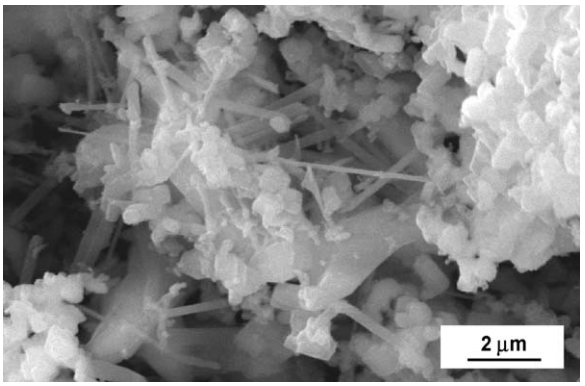

Fig. 7. The SEM micrograph of the product powder (3.9 $m^2\ g^{-1}$) synthesized from SiO_2–5% Y_2O_3 at 1475 °C for 3 h.

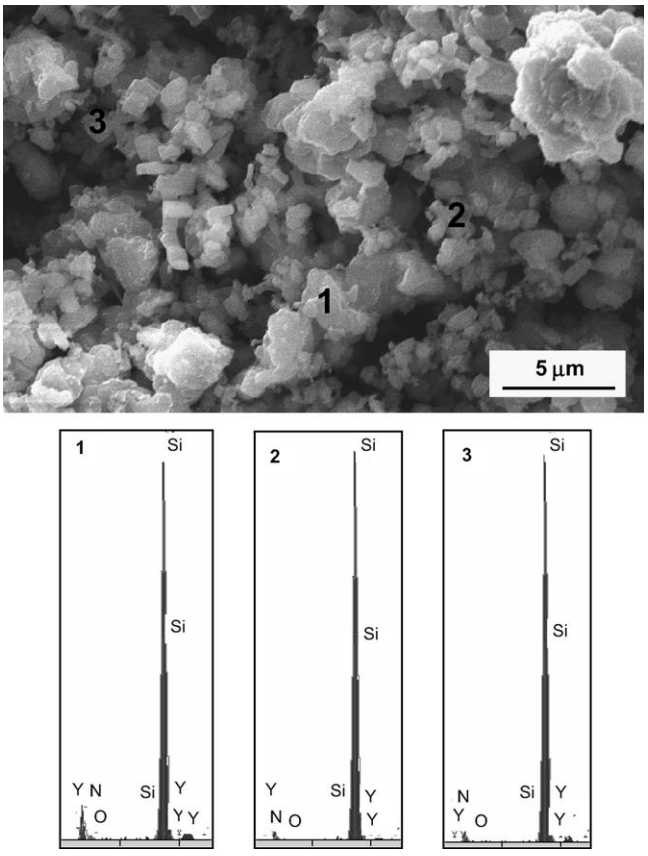

Fig. 8. EDS pattern of the powders synthesized from SiO_2–5% Y_2O_3 at 1475 °C for 3 h.

4. Conclusions

Small grains of α-silicon nitride (α-Si_3N_4) powders with a surface area of up to 4.73 $m^2\ g^{-1}$ were successfully synthesized by the carbothermal reduction–nitridation of a mixture of SiO_2 containing pre-additives of MgO and Y_2O_3 at 1450 and 1475 °C, respectively. The time to complete the reaction was only 3 h. Si_3N_4 having various morphologies with different sintering aids (MgO or Y_2O_3) can be produced by changing the starting powders types and amounts of additives and by altering the process parameters. In general, the powders showed two major morphologies: sub-micron equiaxed and long–short whiskers.

Acknowledgements

The authors wish to acknowledge funding from DPT (State Planning Organization of TURKIYE—Grant No. DPT-2003K120970). We thank EGE Kimya A.Ş. for their help in providing raw materials.

References

[1] K. Houjou, K. Ando, M.C. Chu, S.P. Liu, S. Sato, Effect of sintering additives on the oxidation behavior of Si_3N_4 ceramics at 1300 °C, J. Eur. Ceram. Soc. 25 (2005) 559–567.
[2] H.T. Lin, M.K. Ferber, Mechanical reliability evaluation of silicon nitride ceramic components after exposure in industrial gas turbines, J. Eur. Ceram. Soc. 22 (2002) 2789–2797.
[3] V. Pavarajarn, T. Vongthavorn, P. Praserthdam, Enhancement of direct nitridation of silicon by common metals in silicon nitride processing, Ceram. Int. 33 (2007) 675–680.
[4] A. Demir, Z. Tatli, F. Caliskan, A.O. Kurt, Carbothermal reduction and nitridation of quartz mineral for the production of alpha silicon nitride powders, Mater. Sci. Forum 554 (2007) 163–168.
[5] M.D. Alcala, J.M. Criado, C. Real, Influence of the experimental conditions and the grinding of the starting materials on the structure of silicon nitride synthesised by carbothermal reduction, Solid State Ionics 141 (2001) 657–661.
[6] M. Oliveira, S. Agathopoulos, J.M.F. Ferreira, The influence of Y_2O_3-containing sintering additives on the oxidation of Si_3N_4-based ceramics and the interfacial interactions with liquid Al-alloys, J. Eur. Ceram. Soc. 25 (2005) 19–28.
[7] G. Ling, H. Yang, Pressureless sintering of silicon nitride with magnesia and yttria, Mater. Chem. Phys. 90 (2005) 3–34.
[8] S. Kurama, M. Herrmann, H. Mandal, The Effect of processing conditions, amount of additives and composition on the microstructures and mechanical properties of α-sialon ceramics, J. Eur. Ceram. Soc. 22 (2002) 109–119.
[9] X.J. Liu, Z.Y. Huang, Q.M. Ge, X.W. Sun, L.P. Huang, Microstructure and mechanical properties of silicon nitride ceramics prepared by pressureless sintering with MgO–Al_2O_3–SiO_2 as sintering additive, J. Eur. Ceram. Soc. 25 (2005) 3353–3359.
[10] M. Gopal, L.C. De Jonghe, G. Thomas, Silicon nitride joining using rare-earth reaction sintering, Scripta Mater. 36 (1997) 455–460.
[11] A.O. Kurt, T.J. Davies, Synthesis of Si_3N_4 using sepiolite and various sources of carbon, J. Mater. Sci. 36 (2001) 5895–5901.
[12] R. Koc, S. Kaza, Synthesis of α-Si_3N_4 from carbon coated silica by carbothermal reduction and nitridation, J. Eur. Ceram. Soc. 18 (1998) 1471–1477.