UDK 621.762.5:666.3/.7
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 48(2)171(2014)

SYNTHESIZING Si_3N_4 FROM A MIXTURE OF SiO_2-CaO

SINTEZA Si_3N_4 IN MEŠANICE SiO_2-CaO

Nuray Karakuş, Hüseyin Özkan Toplan
Sakarya University, Engineering Faculty, Dept. of Metallurgy and Materials Engineering, 54187 Sakarya, Turkey
nurayc@sakarya.edu.tr

Prejem rokopisa – received: 2012-08-16; sprejem za objavo – accepted for publication: 2013-07-05

In this study α-phase-rich Si_3N_4 powders were synthesized containing the sintering additive (CaO) using carbothermal reduction and nitridation. The starting agent for the silicon source was high-purity (99 %) synthetic silica. Carbon was added to the high-purity SiO_2 above the stoichiometric amount of oxygen. $CaCO_3$ (for the silicon nitride containing the mass fraction of CaO w = 10 %) was premixed in the starting reactants depending on the final powder composition and the type and amount of the secondary phases required for sintering. The synthesis was carried out in a tube furnace in different temperature ranges (1400 °C, 1450 °C and 1475 °C for 3h) under a nitrogen-gas atmosphere. Having completed the synthesis process, the powder properties were examined using standard characterization techniques (XRD, SEM, etc.).

Keywords: silicon nitride, carbothermal reduction, CaO, SiO_2

V tej študiji so bili sintetizirani s karbotermično redukcijo in nitridacijo z α-fazo bogati prahovi Si_3N_4 z dodatkom za sintranje (CaO). Začetni izvir silicija je bil zelo čisti (99 %) sintetični SiO_2. Ogljik je bil dodan zelo čistemu SiO_2 nad stehiometrično količino kisika. $CaCO_3$ (za silicijev nitrid je vseboval 10 % CaO) je bil primešan začetnim reaktantom, odvisno od končne sestave prahu in vrste ter količine sekundarnih faz, potrebne za sintranje. Sinteza je bila izvršena v cevni peči pri različnih temperaturah (1400 °C, 1450 °C in 1475 °C, 3 h) v atmosferi dušika. Po sintranju so bile lastnosti prahu ugotovljene z uporabo navadnih tehnik za karakterizacijo (XRD, SEM itd.).

Ključne besede: silicijev nitrid, karbotermična redukcija, CaO, SiO_2

1 INTRODUCTION

Silicon nitride (Si_3N_4) ceramics have a range of structural applications, such as engine components, heat exchangers, pump-seal materials, ball bearings, cutting tools, etc., owing to their excellent mechanical properties at both room and elevated temperatures.[1] The material properties of Si_3N_4 have led to speculation that it may also have a role in biomedical fields, since it is biocompatible and is visible on plain radiographs as a partially radiolucent material.[2]

The most common methods for silicon nitride preparation are the carbothermal reduction and nitridation (CRN) of silica, the direct nitridation of silicon and the thermal decomposition of silicon diimide. The carbothermal reduction used in this study takes place according to the following overall reaction:[3]

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO \qquad (1)$$

One of the difficulties found in the fabrication process is the sintering applied to attain high relative densities. Therefore, the use of additives to form a liquid phase is required.[4] Sintering aids such as MgO, Y_2O_3 and Al_2O_3 added to α-Si_3N_4 powders must be homogeneously distributed and possess the desired powder composition before shaping and sintering.[5] In this study α-phase-rich Si_3N_4 powders were synthesized containing a sintering additive using carbothermal reduction and nitridation. Thus, Si_3N_4 powder is ready for sintering and in addition is produced in a single step. Calcium oxide (CaO) was chosen as a metal oxide additive and it was mixed before synthesizing the Si_3N_4. Silicon nitride ceramic powders synthesized using this method might therefore be readily sintered because homogeneously distributed sintering additives were present in the starting materials. For this reason, the processing parameters are described in terms of the powder-synthesis conditions.

2 EXPERIMENTAL

For the CRN process, the raw material was high-purity synthetic silica of nearly colloidal range and it was supplied from EGE Kimya A. S. Activated charcoal was used as a reducing agent and it was supplied by TÜPRAŞ (Turkish Petroleum Refineries Co). The properties of the silica are given in **Table 1**. $CaCO_3$ was used as the CaO source; it was supplied by Çelvit Company. The $CaCO_3$ (for the silicon nitride containing w = 10 % CaO) was premixed in the starting reactants, depending on the final powder composition and the type and amount of the secondary phases desired for sintering. Carbon was added to the high-purity SiO_2 above the stoichiometric amount of oxygen (w(C)/w(SiO_2) ratio of 3). Dry mixing was performed by ball milling for 10 h with alumina

Table 1: Properties of silica (with firm data)
Tabela 1: Lastnosti SiO_2 (podatki dobavitelja)

Properties	SiO_2
Purity (%)	99
Grain size (µm)	14
Specific surface area (BET) ($m^2\ g^{-1}$)	139

balls for the composition. The nitrogen gas (99.99 % in purity) that was used for the nitridation process was supplied by BOS.

The carbothermal reduction and the nitridation process (CRN) were carried out in an atmosphere-controlled tube furnace. The synthesis was performed under a nitrogen gas flow (1 L/m) at 1400 °C, 1450 °C and 1475 °C for 3 h. After holding at these temperatures and this time, the furnace was allowed to cool to room temperature. The gas flow was stopped during cooling when the temperature reached 900 °C. After the CRN process, the products were heated in air for 1 h at 900 °C for residual carbon burning.

After the CRN process at different temperatures, the powder properties were examined by using standard characterization techniques (XRD, SEM, EDS).

3 RESULTS AND DISCUSSION

The silica was mixed with w(CaO) = 10 % (based on the final product) and carbon black for the CRN process. The prepared mixture was subjected to the CRN process for 3 h at 1400 °C, 1450 °C and 1475 °C. The XRD analyses of the produced powders are shown in **Figure 1**.

The α-Si_3N_4 was formed at a temperature of 1400 °C after 3h of reaction. In addition, small amounts of unconverted SiO_2 and CaN_2O_3 phase were found in the product powders. The temperature was increased to 1450 °C, but the β-Si_3N_4 formation was not completed at this temperature, which indicates that the holding time and/or temperature were not enough to complete the reaction. The best result was obtained at 1475 °C after a 3 h reaction. At this temperature (1475 °C), the produced powder was converted to α-Si_3N_4 and β-Si_3N_4, and in addition a minor amount of $CaSi_2N_2O_2$ was present. The formation of the $CaSi_2O_2N_2$ phase by a solid-state reaction was completed at 1300–1400 °C for 10 h.[6,7]

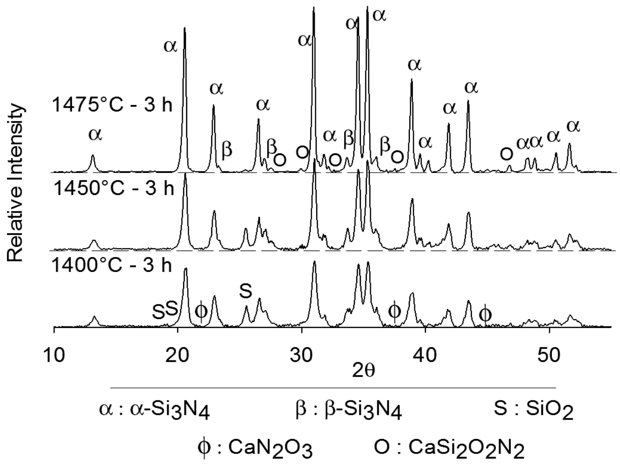

Figure 1: Phases formed at different temperatures (1400–1475 °C) after CRN of the SiO_2 – w(CaO) = 10 % mixture

Slika 1: Faze, ki nastajajo pri različnih temperaturah (1400–1475 °C) po CRN mešanice SiO_2 in w(CaO) = 10 %

The complete formation of α-Si_3N_4 without using an additive (without CaO) was obtained at 1475 °C for a 6 h reaction, but the β-phase was not dedicated.[8] As seen from the XRD data, the carbothermal reduction and nitridation took place at 1475 °C. Comparing this with our previous work, the optimum temperature is the same for the product powders that used Y_2O_3 and Y_2O_3-Li_2O and 25 °C higher than the products that used MgO.[9] The powder produced at 1475 °C was fully converted to α and β-Si_3N_4, and a minor amount of $CaSi_2N_2O_2$ phase, as expected, were present. Different types of additives have been employed for the pressureless and pressure-assisted sintering of Si_3N_4 ceramics.

The melting temperature of the CaO-SiO_2 system is approximately 1436 °C, as indicated by the binary phase-equilibrium diagram.[10] However, the presence of N lowers these eutectic temperatures further. The alkali and alkaline-earth oxides have a low melting point and the viscosity of the resulting liquid is also low. The solution-diffusion-precipitation processes are enhanced.[11] Therefore, the $CaSi_2N_2O_2$ phase obtained after the CRN process can be desirable as the sintering aids for later use in sintering. Studies on the sintering of these synthesizing powders will be the focus of future work.

SEM micrographs of the powder synthesized from SiO_2 – w(CaO) = 10 % at 1400 °C and 1475 °C for 3 h are given in **Figure 2**. The micron-sized Si_3N_4 grains

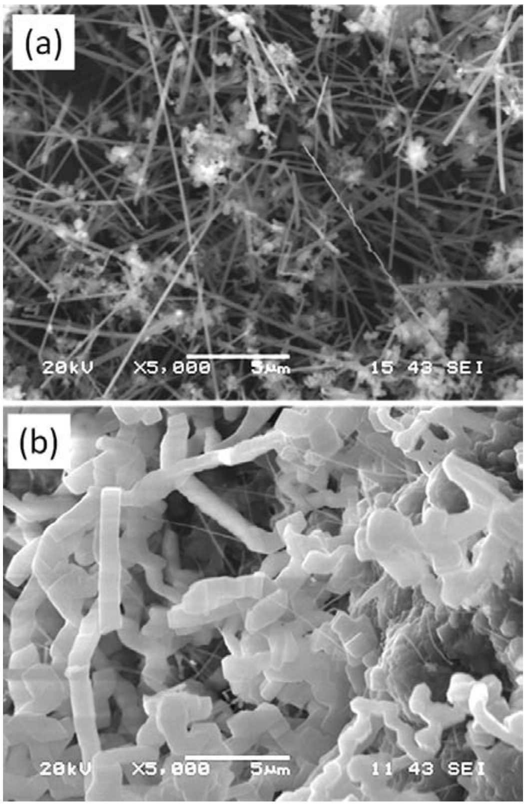

Figure 2: SEM micrographs of the product powder synthesized at: a) 1400 °C, 3 h and b) 1475 °C, 3 h

Slika 2: SEM-posnetka prašnatega produkta, sintetiziranega pri: a) 1400 °C, 3 h in b) 1475 °C, 3 h

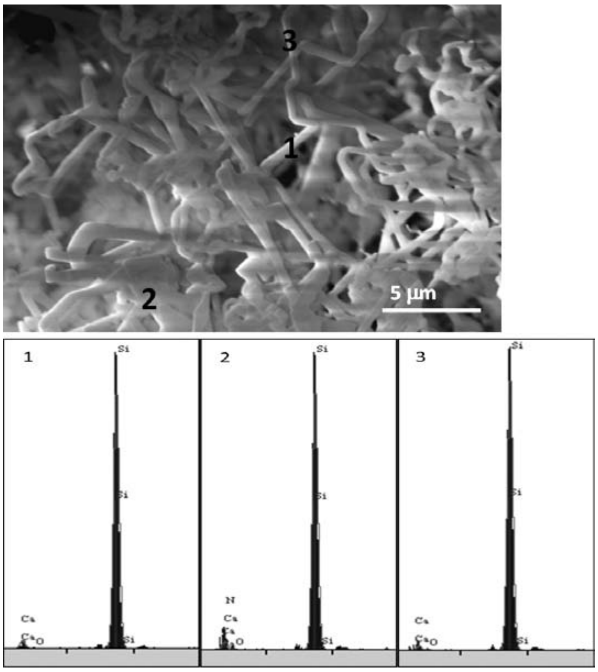

Figure 3: EDS analysis of the powders synthesized from SiO_2 – w(CaO) = 10 % at 1475 °C for 3 h

Slika 3: EDS-analiza prahov, sintetiziranih iz SiO_2 – w(CaO) = 10 % pri 1475 °C po 3 h

were formed after the CRN. SEM micrographs of the powder produced at 1400 °C for 3 h revealed different morphologies, ranging from irregular-shaped small particles to equiaxed small grains and long whiskers. The long whiskers had a cross-section of approximately 300 nm. SEM micrographs of the produced powder at 1475 °C for 3 h revealed the same morphologies as small particles and long whiskers.

It was clear that the grain size was increased with increasing temperature from 1400 °C to 1475 °C. The whiskers had a thickness of approximately 1 µm after the CRN process at 1475 °C. The EDS analysis of the powders synthesized from SiO_2 – w(CaO) = 10 % at 1475 °C for 3 h is showed in **Figure 3**. According to the EDS analysis, the Si, N, O, and Ca elements were detected from the particles in a manner consistent with the XRD analysis (**Figure 1**).

4 CONCLUSIONS

α-Si_3N_4 powders containing CaO as an oxide additive were successfully synthesized by carbothermal reduction and nitridation. The best result was obtained at 1475 °C after a 3 h reaction. The Si_3N_4 powders showed two major grain morphologies: submicron equiaxed and long whiskers. The advantage of using pre-additive oxide (CaO) in the CRN process is in terms of the reaction temperature and time.

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