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Synthesis of the in-Situ Si₃N₄-SiC Composite Nano Powders by Carbothermal Reduction

F. ÇALIŞKAN^{a,*}, E. KOCAMAN^b AND S. CÖMERT^a

^aSakarya University, Faculty of Technology, Department of Metallurgical and Materials Engineering

^bBulent Ecevit University Faculty of Engineering Department of Metallurgical and Materials Engineering

Si₃N₄-SiC micro-nano composite powder has been studied by a group of authors during the last decade. Previous works have shown that SiC-Si₃N₄ ceramics exhibits good mechanical properties and high corrosion resistance at elevated temperatures. In this study, we have tried a new approach to obtaining SiC-Si₃N₄ ceramic composite powder by changing the conditions in the carbothermal reduction process. Starting powders were quartz mineral, received from Ege-Sil Co., as silicon-source and, carbon, as silica-reducing and carburizing agent. These powders were ground in the ring mill, separately and together. Carbothermal reduction-nitridation/carburization reactions were carried out in a tube furnace at > 1400 °C for 4 hours under N₂ and Ar gas, used as nitriding and shielding atmosphere. The synthesized powders were characterized by X-ray diffraction, SEM, and EDS. Results have shown that production of Si₃N₄-SiC micro-nano composite powder was achieved in the modified nitrogen and argon atmosphere above 1400 °C. Determination of the Si₃N₄/SiC ratio was possible with sensitive control of the system conditions.

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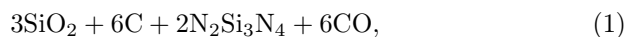
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1. Introduction

Synthesis and mechanical properties of Si₃N₄/SiC micro/nano composites have been studied by a number of authors during the last 15 years [1]. Increased scientific attention to ultra-fine grained ceramics has been derived by the promise of a reduction in flaw sizes, enhanced superplasticity, and the promise of improvement of a wide variety of other properties, as the grain size shrinks to nanometric dimensions [2–4]. Nano/micro and nanoceramics have some advantages, such as high-temperature strength and better creep resistance compared to monolithic ceramics [5–9]. Silicon carbide and silicon nitride have different mechanical properties. Si₃N₄ shows high fracture toughness but exhibits low oxidation resistance at high temperature. In contrast, SiC displays high oxidation resistance at high temperature [10–13].

Ceramic composites are grouped into two categories; micro composites and nano composites [2]. Micro-composites usually have been used to improve fracture toughness by dispersing micro size second phases, such as particulates, platelets, whiskers and fibers. On the other hand, nanocomposites can be divided into three categories; intragranular, intergranular composites and nano/nano composites. In these types of ceramics the aim is to improve not only the mechanical properties such as hardness, fracture strength and toughness and reliability at room temperature, but also high-temperature mechanical properties, such as hardness, strength, and creep and fatigue fracture resistances [14–20].

The main processing routes for the synthesis of Si₃N₄ and SiC powders are a carbothermic reduction of silica or silicon-based materials by carbon and subsequent nitridation by N₂ or NH₃, thermal chemical vapor deposition (CVD), plasma (PCVD), polymer pyrolysis and high energy reaction milling [20–24]. Silicon nitride (Si₃N₄) and silicon carbide (SiC) powders can be synthesized from silica SiO₂ via the carbothermal reduction process in the presence of nitrogen or argon, according to overall reactions:



Above reactions have endothermic character, 1268 kJ/mol for Si₃N₄ and 572 kJ/mol for SiC at 1427 °C and 1827 °C, respectively [25–26]. Silicon carbide is a stable specie under coexistence with carbon, above 1500 °C, for $P_{\text{N}_2} = 1$ atm. Within a relatively narrow temperature window around this transition temperature, SiC grain growth is minimized and nanophase SiC crystallites are produced. It is in this temperature range that nanophase SiC/Si₃N₄ composite powders can be synthesized [25–26]. In this study, a different route from conventional methods was tried in order to synthesise micro/nano powders. Synthesis of silicon nitride and silicon carbide composite powder took place using the modified carbothermal reduction process, which uses gradual conversion in the presence of nitrogen and argon.

2. Experimental

In this study, SiC-Si₃N₄ composite was obtained in a vertical tube furnace, which consists of a recrystallised alumina tube 100 mm in length, 60 mm in

*corresponding author; e-mail: fcaliskan@sakarya.edu.tr

diameter, at $> 1450^{\circ}\text{C}$ for 4 h. The composition of starting powder was SiO_2 (min 98 wt.%, main phase), max. 2 wt.% impurity, max. 0.05 wt.% metallic Fe (Ege Kimya Company, Turkey). SiO_2 powder has particle sizes of $d(0.1) = 4.892 \mu\text{m}$, $d(0.5) = 13.490 \mu\text{m}$ and $d(0.9) = 34.003 \mu\text{m}$, for the raw material. The calculated specific surface area of the SiO_2 powder was $0.67 \text{ m}^2/\text{g}$. Carbon was used as a reducing agent (CABOT, Vulcan XC 72).

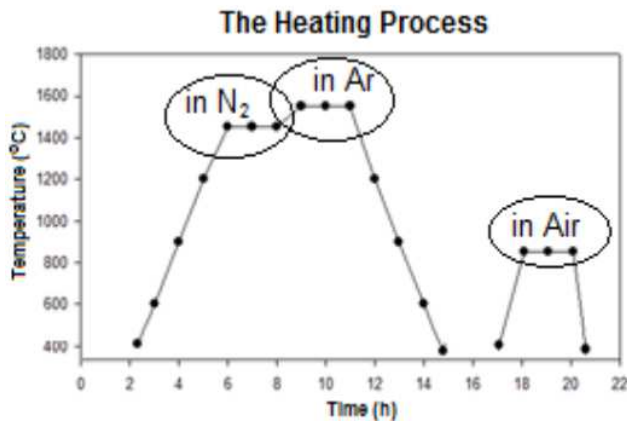


Fig. 1. Thermal process of the modified CRNC conversion.

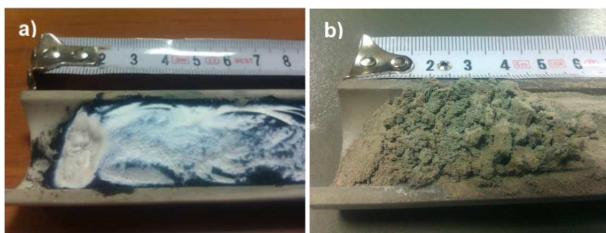


Fig. 2. a) Sample after CRN-CR, b) sample after carbon burning out.

As can be seen in Fig. 1, the conversion process was modified and was carried out gradually in two steps. The first step was carried out under N_2 at 1450°C for 2 h. During the heating process, nitrogen was flowing into the furnace both to react with free silicon and to protect the carbon against oxidation. Ar was introduced only to protect the reactants against oxidation. The next step occurred under Ar atmosphere at 1550°C during 2 h. While the aim of the first step was to obtain the partial conversion to silicon nitride powder, the goal of the second step was to synthesize silicon carbide powder from the unreacted silica. The stoichiometric ratio was 3:1 (wt.) between SiO_2 and carbon. We needed to know whether the CRNC conversion was completed or not. The first indicator of achievement of the conversion is a change in color of the yielded powder. Figure 2 shows that there is a color change of the powder mixture from black to white-grey tones. The resulting product of a khaki-color was obtained by the burn-out of excess carbon.

The products were heated in air for 1 h at 900°C for residual carbon burning after carbothermal reduction nitridation and carburization (CRNC) process. The yield powders were analyzed (Rigaku, D/MAX/ 2200/PC, Japan) using X-ray diffraction method (XRD), $\text{Cu K}\alpha$ radiation source ($\lambda = 1.540456 \text{ \AA}$), to identify the obtained phases and using a scanning electron microscopy (SEM), to investigate grain morphology. Energy dispersive spectrometer (EDS) integrated with SEM was used to determine the elemental composition.

3. Results and discussion

3.1. Scanning electron microscopy of the yield powder

The CRN product, as shown in the SEM micrograph in Fig. 3, consists of fibrous particles $0.1\text{--}1 \mu\text{m}$ in diameter and $< 10 \mu\text{m}$ in length. Si_3N_4 powder has high aspect ratio fibrous particles. The SEM micrograph in Fig. 4 shows ultra-high aspect ratio particles (approx. $l/d = 80\text{--}100$). As seen in Fig. 4, the SiC nanorods typically have diameters of $\sim 100 \text{ nm}$ and lengths of $< 10 \mu\text{m}$.

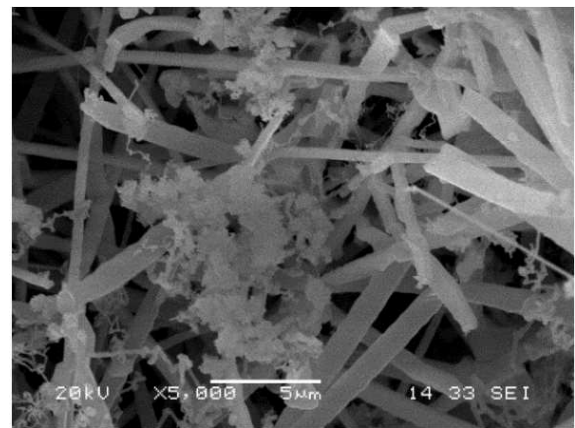


Fig. 3. Si_3N_4 particles after CRN at 1450°C for 4 h.

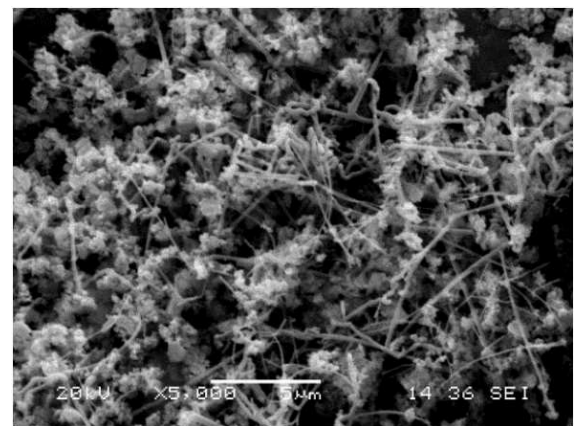


Fig. 4. SiC particles after CRN at 1550°C for 4 h.

Both the SiC nanorods and the Si_3N_4 fibrous particles are generally straight and have a preferential axis orientation, as shown in Figs. 3 and 4.

Y.H. Gao et al. have found that the axis orientation of the SiC was constant along the length of the nanorod [27]. To synthesize the SiC-Si₃N₄ in situ composite, the powder mixture prepared with a stoichiometric ratio was heat treated in two steps, which was explained in detail in the Experimental section. When the SEM micrograph (Fig. 5) of the obtained in situ composite powder was handled to observe the difference between monolithic Si₃N₄ and monolithic SiC particles, it became clear that the SiC particles have a superior aspect ratio when compared with Si₃N₄ particles. While the SiC rods are very fine, of nano size, the Si₃N₄ fibers are of submicron size. The authors think that the simultaneous conversion of the same substrate, SiO₂, provides a considerable advantage, which is, that the process can result in perfectly bonded fiber-matrix interface after sintering.

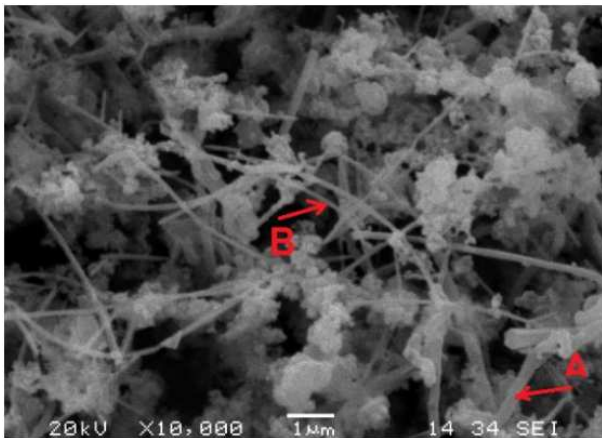


Fig. 5. Simultaneous conversion to SiC+Si₃N₄ composite powders after the CRNC with mix process conditions.

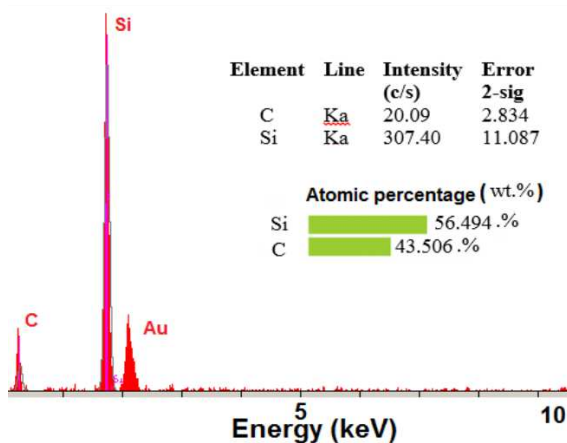


Fig. 6. EDS analysis of A point from Figure 5.

As shown in Fig. 6, the EDS analysis of A point from Fig. 5 reveals that this particle consists of only Si and N elements, which means it is Si₃N₄. Au peak arises from the coating material which was deposited to increase the conduction. The EDS analysis (Fig. 7) of B point from

Fig. 5 reveals that this rod is a SiC particle. In the SiC nanoparticles, only Si and C can be detected using EDS analysis.

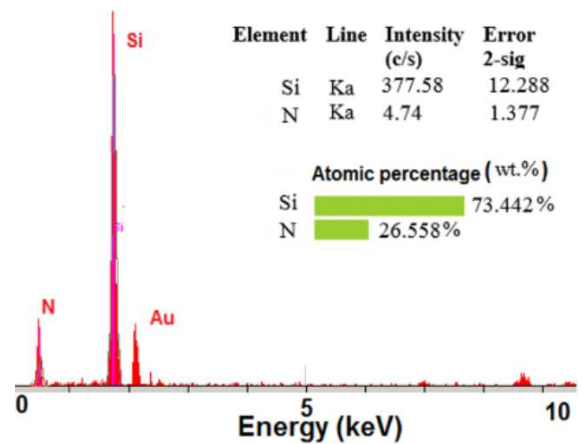


Fig. 7. The EDS analysis of B point from Figure 5.

3.2. PXRD analysis results

Diffraction pattern in Fig. 8 belongs to the CRNC product. The results show that there are no other phases except β -SiC and α -Si₃N₄. The conversion, from SiO₂ to SiC-Si₃N₄, was fully achieved above 1450 °C. The XRD diagram does not contain any peaks from other phases. The product has high purity in terms of impurity phase content, beta silicon nitride included as well. The amounts of relative phases were determined using the XRD data. The composite powder consists of 45% of β -SiC and 55% of α -Si₃N₄. It was obvious that there was nearly 10% difference in the amount of the SiC and the Si₃N₄. In this case, Si₃N₄ can be accepted as matrix phase. This result demonstrates that the in-situ SiC-Si₃N₄ composites can successfully be synthesized in the same process in two steps.

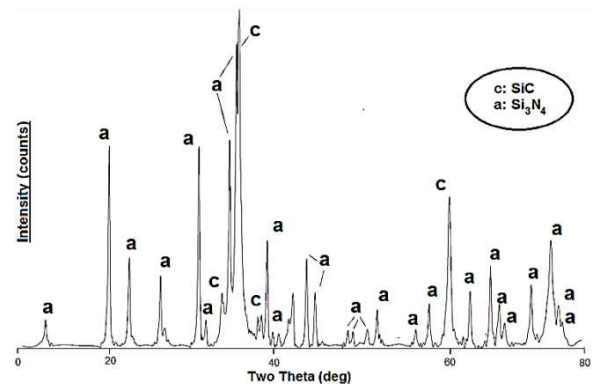


Fig. 8. X-ray diffraction patterns of the composite powder produced in the modified process.

4. Conclusions

The work was focused on the production of the in-situ Si₃N₄-SiC composite powder, using the CRNC. This aim

was achieved gradually by the modified carbothermic reactions at 1450 °C and 1550 °C, respectively, for totally 4 h. SiC nanorods 100 nm in diameter and max. 10 μm in length have been synthesized by a CRNC reaction. While, $\alpha\text{-Si}_3\text{N}_4$ was obtained, in Fig. 2, by the CRN, silicon carbide was synthesized, in Fig. 3, by the CRC. The in situ $\text{Si}_3\text{N}_4\text{-SiC}$ nano fiber composite powder was achieved in a powder batch through the modified CRNC process. Authors think that a sintered ceramic body using the produced $\text{Si}_3\text{N}_4\text{-SiC}$ composite powder will exhibit superior mechanical properties, such as better hardness, higher toughness, higher compressive strength etc., than those of the conventional powders. This process is inexpensive to use for production of very fine advanced ceramic powder both separately and together. In addition, the main difficulties of fabrication of a ceramic matrix composite, with homogeneous distribution of reinforcement in the matrix and the mismatch between the nano reinforcement, were minimized using the presented CRNC process.

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