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Cost-effective synthesis of Si_3N_4-SiC nanocomposite powder

A. ŠAPONJIĆ, B. MATOVIĆ, B. BABIĆ, J. ZAGORAC, V. POHARC-LOGAR[a], M. LOGAR[a]
Institute of Nuclear Sciences „Vinča“, P.O. Box 522, 11001 Belgrade, Serbia
[a]Faculty of Mining and Geology, University of Belgrade, Djusina 7, 11000 Belgrade, Serbia

A carbothermal reduction and nitridation process (CRN) was employed to prepare Si_3N_4-SiC nanocomposite powder [1-4]. Diatomaceous earth from Serbian deposite was used as Si precursor in the synthesis of nanocomposite powder by mixing with commercial sugar as reduscing agent. Purified diatomaceous earth with pre-determined C/SiO_2 ratio of 5 yuilded Si_3N_4-SiC nanocomposite powder. The XRD (Rietveld analysis) was employed to evaluate Si_3N_4/SiC ratio of the obtained powder after CRN. Also IR and SEM analysis were used to determine morphology and chemical composistion. The results show that the optimally temperature was 1450 °C, which is wery low, compared to the classical synthesis process.

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1. Introduction

Carbothermal-reduction and nitridation process (CRN) is promissing candidate for obtaining a large variety of non-oxides products with important technical uses. The synthesis of either pure Si_3N_4 / SiC powders or nanocomposite powders Si_3N_4 - SiC is one of the important factors for obtaining dense non-oxide technical ceramics [5]. Although the quality and performance are important, the cost of mass production should be the key factor in the commercialization of non-oxide ceramics [6]. The process involves reduction of oxygenated materials, such as silica (SiO_2) usually by mixing with a reducing agent (carbon) in excess at the temperature higher than 1600 °C for several hours under an inert atmosphere. Formation of final product is very complex and demands many intermediate stages [7]. This procedure offers the possibility of an economically attractive production route from naturally occurring materials.

Diatomaceous earth is a natural occurring mineral compound formed of microscopic skeletal remains of unicellular algae-like plants called diatoms. Diatom particles have pitted surface area which is several times greater than any other natural compound with the same particle size. The surfaces of diatom frustules possess fine pores with dimensions ranging from the micro scale to the nanometer scale. Such high surface area and siliceous composition can be used as Si precursor for the synthesis of SiC powder by carbothermal-reduction reaction (CRR) by mixing with one of reducing agents.

Different processing techniques have been applied for the preparation of Si_3N_4/SiC composites [8-10]. In most cases the mixing of two powders (Si_3N_4 and SiC) and their sintering is the common technique. However, the problem with homogenization is always present. Better solution might be to use the composite powders obtained in situ. Carbothermal-reduction and nitridation process allows in situ synthesis of mixture of non-oxide powders (Si_3N_4/SiC), which should have a number of advantages compared to pure powders due to its low-cost, narrow particle size and ideal homogeneity.

Many authors studied the formation of non-oxide powders from various minerals such as different types of clays [11-16]; sepiolite [17], serpentine [18], mountain leather asbestos [19] as well as from aluminosilicates and bauxite [20]. Among the raw materials that may be used for non-oxides production, the diatomaceous earth shows some advantages such as: low price, high specific surface area and high silica content.

2. Experimental

2.1. Starting materials

The raw material used was a diatomaceous earth from the Serbian deposit (Kolubara, basin). In order to reduce impurities content from raw material, diatomaceous earth was previously acid treated with HCl solution of 1 mol dm^{-3} concentration. The chemical composition of as-received and chemically treated diatomaceous earth are determined by wet chemical methods (Table 1).

Table 1. Chemical composition of as-received diatomaceous earth and the chemically treated diatomite.

Oxides	As-received sample	Chem. Treated sample
SiO_2	73.68	76.58
Al_2O_3	12.28	11.34
Fe_2O_3	3.29	1.72
CaO	0.72	1.22
MgO	0.44	0.44
K_2O	1.01	0.9
Na_2O	0.12	0.11
L.O.I. (1000°C)	8.26	7.13

After purification, content of Fe_2O_3 and Al_2O_3 was reduced.

As mentioned above, as a source of carbon commercial sugar was used.

2.2. Preparation of mixtures

Mixtures of diatomaceous earth with commercial sugar was obtained by dissolving sugar with appropriate solvent (sugar / distilled H_2O) using magnetic stirrer. Diatomaceous earth was soaked in this solution containing carbon precursor, homogenized with magnetic stirrer and dried until total vaporization of distilled H_2O h at 110 ºC. Starting mixture was obtained after carbonization at 1000 ºC in nitrogen flow for 4 h. Mixture of constant molar ratio of C/SiO_2 (5/1) was homogenized by vibro-milling for 2 h in the presence of distilled water. The green bodies were held in a graphite boat which was placed in an alumina reactor of atmosphere-controlled tube furnace in nitrogen flow. Heat treatment was at the temperatures between 1250 and 1550 ºC for 1, 2 and 4 h. The nitrogen gas used contained less than 5 ppm O_2 and H_2O. In all experiments a N_2 flow of 0.05 $l \cdot min^{-1}$ was used.

The nitrogen flow was kept during cooling till 200 ºC. The excess carbon of the reaction products was removed from samples by oxidation in air at 700 ºC for 4 hours.

2.3. Characterization of powder mixtures

The adsorption characteristics of diatomaceous earth and carbon samples were determined before and after mixing. Adsorption and desorption isotherms of N_2 were measured at -196 °C using the gravimetric McBain method. The specific surface area, S_{BET}, pore size distribution, mesopore including external surface area, S_{meso}, and micro pore volume, V_{mic}, for the samples, were calculated from the isotherms. Pore size distribution was estimated by applying BJH method [21] to the desorption branch of isotherms and mesopore surface and micro pore volume were estimated using the high resolution α_s plot method [21-23]. For comparison, source of carbon was separately ball milled for 2h in order to determine specific surface areas, S_{BET}, and porosity parameters (S_{meso}, S_{mic}, V_{mic}) after milling.

The reaction products were analyzed by XRD over 2θ range from 10° up to 80° using diffractometer with CuKα as the target. Also, the XRD (Rietveld analysis) was employed to evaluate Si_3N_4/SiC ratio of the obtained powder after CRN. Before the measurement the angular correction was done by high quality Si standard.

The IR spectra were recorded on Perkin-Elmer 597 double beam infrared spectrophotometer, in range 4000-200 cm^{-1}. Pressed pellet technique (KBr) was used. Spectra were recorded on a computer through AD converter with sampling rate 1000 Hz, which made possible precise absorption maxima read out.

Micrographs were obtained with a Philips scanning electron microscope (SEM) at 30 kV accelerating voltage.

3. Results and discussion

3.1 Adsorption characteristics

Specific surface areas calculated by BET equation (experimental 2.3), S_{BET}, calculated porosity parameters (S_{meso}, S_{mic}, V_{mic}) of starting materials are given in Table 2.

Table 2. Specific surface areas of starting materials.

Sample	S_{BET} (m^2/g)
Diatomaceus earth	7
Commercial sugar	4

Results of porous properties of carbon source ball milled for 2h. are listed in Table 3.

Table 3. Porous properties of carbon source ball milled for 2h.

Sample	**S_{BET} (m^2/g)**	**S_{meso} (m^2/g)**	**S_{mic} (m^2/g)**
Carb. sugar	261	15	246

The process of milling increased significantly specific surface area of carbonized comercial sugar. Milling process opened closed micro pores developed during the carbonization.

Table 4 shows BET specific surface areas and mean particle size of starting mixture.

Table 4. Specific surface areas and mean particle size, porous properties of starting mixture.

Sample	**S_{BET} (m^2/g)**	**Mean particle size (μm)**	**S_{meso} (m^2/g)**	**S_{mic} (m^2/g)**	**V_{mic} (cm^3/g)**
starting mixture	141	23.8	8	133	0.06

It is clear that mixing caused significant changes in structure of starting mixture in comparison with starting materials. In the case of mixture - carbonized comercial sugar and diatomaceous earth we obtained micro porous sample.

3.2. X-ray diffraction

XRD patterns of composite samples after constant heat treatments at 1350 ºC and different heating time are given in Fig. 1. XRD patterns of samples after CRN treatment for constant heating time, 4 h, at temperatures from 1250-1550 ºC are given in Fig. 2. In all samples crystobalite (SiO_2) was found to be the principal phase at low temperature (1250 °C). Crystobalite (SiO_2) as the major phase decreases with increasing temperature and it finally disappears at 1450 °C, followed by $\beta-Si_3N_4$, SiC and Si_2N_2O appearance. This behavior can be explained by its consuming for SiC and Si_2N_2O phases formation. Appearance of Si_2N_2O phase (sinoite) is based on the reaction [1]

$$3\ Si + SiO_2 + 2\ N_2 \rightarrow 2\ Si_2N_2O \qquad (1)$$

which involves vapor phases of SiO and N_2 and gives a powderous Si_2N_2O. Appearance of Si_2N_2O phase indicates that prior to the reaction (1) the carbothermal-reduction of SiO_2 occurred according the reactions (2):

$$2\ SiO \rightarrow Si + SiO_2 \qquad (2)$$

SiC phase first appeared after 2 h soaking time, in the sample containing sucrose and carbon black as reducing agents at 1350 °C. This can be explained with the fact that milling process opened closed micro pores developed during the carbonization, (Table 2) and hence the large number of contact places appeared which accelerates reaction (which is beneficial for the further course of the reaction). Also, mixture I was obtained from the solution. In other words, carbon precursor was introduced via solution which allowed its penetration in all free space in diatomaceous earth particles. At 1450°C, 4h, $\beta-Si_3N_4$ and SiC are the principle phases.

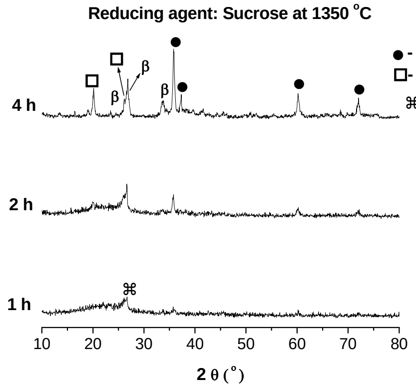

Fig. 1. XRD patterns after constant heat treatments and different heating time, SiO_2-crystoballite.

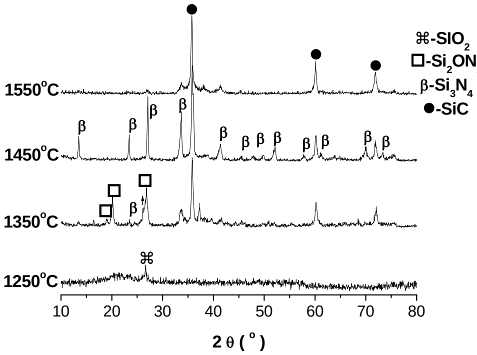

Fig. 2. Comparative XRD patterns after different heat treatments and constant heating time, 4 h of mixture diatomaceous earth-commercial sugar.

Also, at this temperature, $\alpha-Si_3N_4$ should be produced, but the presence of impurities in starting materials produced liquid due to low temperature eutectic reactions which favor the formation of $\beta-Si_3N_4$ instead of $\alpha-Si_3N_4$ [25]. However, at 1550 °C Si_3N_4 phase is unstable in the presence of CO according the reaction:

$$Si_3N_4\ (s) + 3\ CO\ (g) \Rightarrow 3\ SiC\ (s) + 3\ SiO\ (g) + 4\ N_2\ (g)$$

and SiC is the principle phase.

After CRN the XRD (Rietveld analysis) was employed to evaluate Si_3N_4/SiC ratio of the obtained powder. Quantitatively powder obtained at 1450 °C, 4h contains 85,6(6) mass. % of Si_3N_4 and 14,3(1) mass. % of SiC. Crystalline size for Si_3N_4 is: 1407,4(6) Å, and microstrain 0,00143(1).

Comparative IR spectra of samples thermaly treated at 1450 i 1550 °C, 4h are shown in Fig. 3. The band 430 cm^{-1} is commom to $\beta-Si_3N_4$. This band is characteristic of N-Si-N symmetrical bending vibrations. The bands 900, 947 and 1040 cm^{-1} are also commom in $\beta-Si_3N_4$ spectra. These bands are characteristic of Si-N-Si anti-symmetrical stretching vibrations. The band 570 and cm^{-1} is also related with the presence of $\beta-Si_3N_4$.

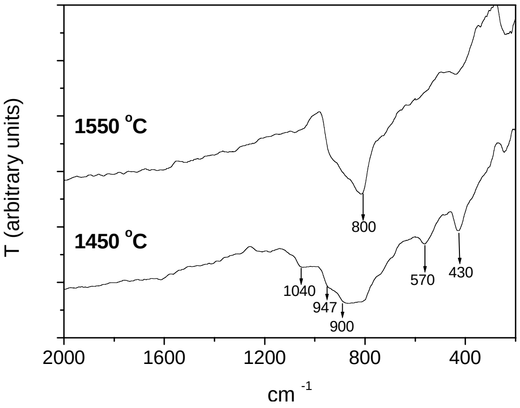

Fig. 3. IR comparative transmission spectra of the mixture after different heat treatments and constant heating time, 4 h of mixture diatomaceous earth-sugar.

At 1550 °C the presence of central mode in the frequency range ~ 800 cm^{-1} enables us to suggest that intensive carbide formation occur at this temperature. These results are in agreement with comparative XRD patterns and confirms that silicon carbide is formed on the account of silicon nitride in the presence of CO.

SEM micrograph of samples obtained after 4 h at 1450°C are given in Fig. 4. The morphology of obtained powders shows that they are highly aggregated. The morphology of powder obtained show that this product retains characteristic of some fragments of the original diatomite similar to honeycomb microstructure.

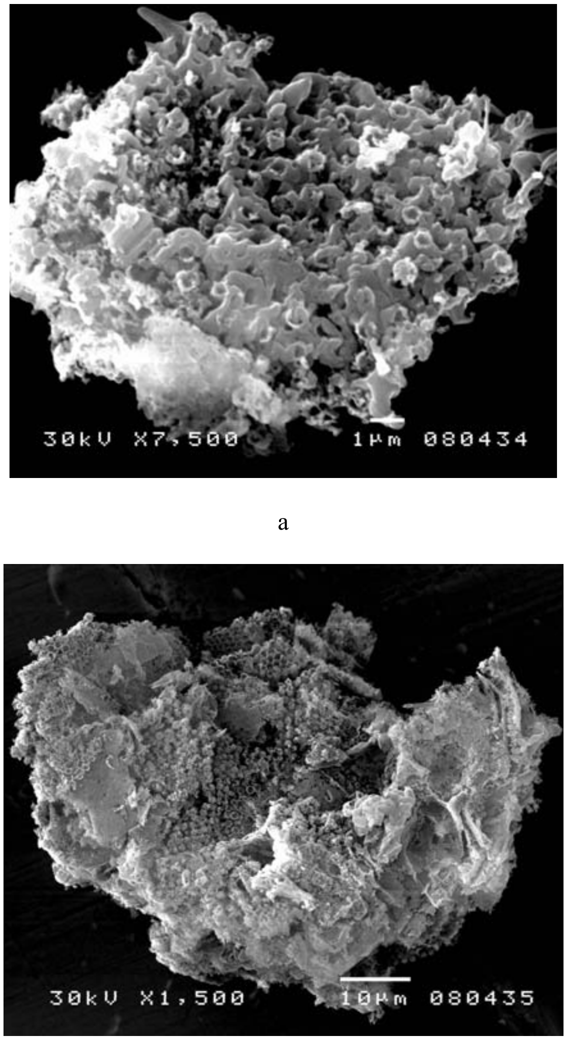

Fig. 4. SEM micrograph of powders obtained after 4 h at 1450°C.

4. Conclusions

This study demonstrated that it is feasible to produce inexpensive non oxide Si_3N_4-SiC powders using diatomaceous earth.

The carbonitriding of diatomaceous earth in low nitrogen flow rate leads to the formation of Si_3N_4/SiC composite powders. According to XRD analyses, the temperature of 1450°C appears to be proper for the synthesis of Si_3N_4/SiC composite powders. The reaction products depend on the reaction temperature and time, where by intermediate compounds appear in small quantities. With increasing temperature, the amount of SiC increases compared to silicon nitride. Powders obtained at higher temperature (1450°C) are the mixtures of silicon carbide and silicon nitride. Results also show that all powders are of nanometric size.

These powders can be used as raw materials for industrial application.

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References

[1] B. Matovic, A. Saponjic, A. Devecerski, M. Miljkovic, J. Mater. Sci. **42**, 5448 (2007).
[2] B. Matovic, A. Saponjic, S. Boskovic, J. Serbian Chem. Soc. **71**, 677 (2006).
[3] H. Arik, J. Eur.Ceram. Soc., **23**, 2005 (2003).
[4] H. Hadjar, B. Hamdi, M. Jaber, J. Brendlé, Z. Kessaïssia, H. Balard, J. B. Donnet, Microporous Mesoporous Mater. **107**, 219 (2008).
[5] K. Komeya, Fine Ceramics, ed. S. Saito, Elsevier Science Publishing Co. New York 1988, p. 175.
[6] A. D. Mazzoni, E. F. Aglietti: Mater. Chem. Phys., **37**, 344 (1994).
[7] D. H. Filsinger, D. B Bourrie, J. Am. Ceram. Soc., **73**, 1726 (1990).
[8] T. Rouxel, F. Wakai, S. Sakaguchi, J. Am. Ceram. Soc. **77**, 3237 (1994).
[9] A. Rendtel, H. Hübner, M. Herrmann, C. Schubert, J. Am. Ceram. Soc., **81**, 1109 (1998).
[10] G. Petzow, M. Herrmann., Structure and Bonding, Springer-Verlag, Berlin **102**, 51 (2002).
[11] J. G. Lee, I. B. Cutler, Am. Ceram. Soc. Bull. **58**, 869 (1979).
[12] Y. Sugahara, K. Kuroda, C. Kato, J. Am. Ceram. Soc. **67**, C-247 (1984).
[13] I. Higgins, A. Hendry, Br. Ceram. Trans. J. **85**, 161 (1986).
[14] A. D. Mazzoni, E. F. Aglietti, E. Pereira, Mater. Lett. **14**, 37 (1992).
[15] A. D. Mazzoni, E. F. Aglietti, E. Pereira, Appl. Clay. Sci. **7**, 407 (1993).
[16] D. Ashkin, J. Eur. Ceram. Soc. **17**, 1613 (1997).
[17] A. O. Kurt, T. J. Davies, J. Mater. Sci. **36,** 957 (2001).
[18] T. W Cheng, C. W. Hsu, Chemosphere **64**, 510 (2006).
[19] A. Devečerski, M. Pošarac, et al., J. Alloys Compd. in press, doi:10.1016/j.jallcom.2007.09.090
[20] A. D. Mazzoni, E. F. Aglietti Chem. Phys. **49**, 196 (1997).
[21] E. P. Barret, L. G. Joyner, P. P. Halenda, J. Am. Chem. Soc. **73**, 373 (1951).
[22] K. Kaneko, C. Ishii, M Ruike, H. Kuwabara, Carbon **30**, 1075 (1992).
[23] M. Kruk, M. Jaroniec, K. P. Gadakaree, J Colloid Interface Sci **192**, 250 (1997).
[24] B. Ž. Matović, S. Bošković, Z. Dohčević-Mitrović, Tech. Acta, **31,** 479 (2000).

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[*] Corresponding author: acavuc@vin.bg.ac.rs