

Carbonitriding reactions of diatomaceous earth: phase evolution and reaction mechanisms

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(Received 14 July, revised 11 November 2005)

Abstract: The possibility of using diatomaceous earth as Si precursor for low temperature synthesis of non-oxide powders by carbothermal reduction-nitridation was studied. It was found that carbonitriding reactions produce phases of the Si–Al–O–N system. Already at 1300 °C, nanosized, non-oxide powders were obtained. The comparatively low reaction temperatures is attributed to the nano-porous nature of the raw material. The evolution of crystalline phases proceeded *via* many intermediate stages. The powders were characterized by X-ray and SEM investigations. The results showed that diatomaceous earth can be a very effective source for obtaining non-oxide powders.

Keywords: carbothermal reactions, precursors, diatomaceous earth, Si₃N₄, sialon.

INTRODUCTION

The carbothermal-nitridation reaction (reduction with carbon and simultaneous nitriding of oxygenated materials) is the most promising candidate for obtaining a large variety of non-oxide products with important technical uses.¹ This reaction offers the possibility of an economically attractive production route from naturally occurring materials. The formation of non-oxide powders from minerals such as different types of clays,^{2–7} sepiolite^{8,9} and from aluminosilicates and bauxite^{10–12} has been studied. Among the raw materials that may be used for the production of non-oxides, diatomaceous earth has some advantages, such as high specific surface area, high silica content and low price.

Diatomaceous earth is a natural occurring mineral compound from microscopic skeletal remains of unicellular algae-like plants called diatoms. As living plants, diatoms weave microscopic shells from silica, however as they die, deposits are formed and fossilized. Diatom particles have a pitted surface, the area of which is several times

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doi: 10.2298/JSC0606677M

greater than any other natural compound having the same particle size. The surfaces of diatom frustules possess fine pores with dimensions ranging from the micro to the nanometer scale. Such a high surface area and siliceous composition can be used as a Si precursor for the synthesis of different types of non-oxide powders by carbothermal reduction-nitridation (CRN) by mixing with a reducing agent.

EXPERIMENTAL

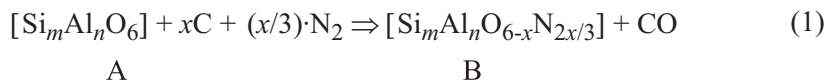
The raw material used was a diatomaceous earth from Serbia. Carbon black with a specific surface area BET = 46 m² g⁻¹ and 99 % purity was used as the reducing agent. The diatomaceous earth was first treated with a 1 mol/dm³ HCl solution in order to remove iron oxide from the material. The chemical compositions of the as-received and chemically treated samples were determined by wet chemical methods (Table I). Mixtures of different C/SiO₂ ratios were homogenized by vibro milling in the presence of distilled water. The green bodies were heated at temperatures between 1200 and 1500 °C in an alumina reactor under a controlled nitrogen flow. The employed nitrogen gas contained less than 5 ppm O₂ and H₂O. In all experiments, a N₂ flow of 0.51 min⁻¹ was used. The alumina reactor was heated in a furnace with a SiC heating element. The temperature was measured with Pt-(Pt-10 wt.% Rh) thermocouple (± 5 °C). The nitrogen flow was maintained during cooling 200 °C. The reaction products were analysed by XRD over the 2θ range 10° to 90° using a diffractometer with CuKα as the target. Micrographs were obtained with a Philips scanning electron microscope (SEM).

TABLE I. Chemical composition of the as-received diatomaceous earth and the chemically treated diatomite

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	L.O.I (1000 °C)	Sample
73.68	12.28	3.29	0.72	0.44	1.01	0.12	8.26	As-received
76.58	11.34	1.72	1.22	0.44	0.9	0.11	7.13	Chem. treated

RESULTS AND DISCUSSION

According to its shape and morphology the as-received raw material belonged to the Aulacoseira type of diatoms (Fig. 1). The diatom particles possessed a pitted surface with fine pores of dimensions ranging from the micro to the nanometer scale. Its XRD pattern showed that the main mineralogical component was crysallite (SiO₂), accompanied by an amorphous phase. The chemical composition showed that the diatomaceous earth was mainly composed of SiO₂ with significant quantities of Al₂O₃. Other impurities, such as Na₂O, K₂O and Fe₂O₃, were also present. However, it is known that Na₂O and K₂O are largely lost during the carbothermal reduction stage. On the other hand, it would be expected that Fe₂O would be reduced to Fe or iron silicides (FeSi), but small quantities of iron has been shown to help initialize the nitridation.¹³ Thus, the phase relation during the carbonitridation reaction of diatomaceous earth (a mixture of silica and alumina) may be derived from the quaternary system Si–Al–O–N (Fig. 2). Thus, the overall reaction may be represented by the equation:¹⁴



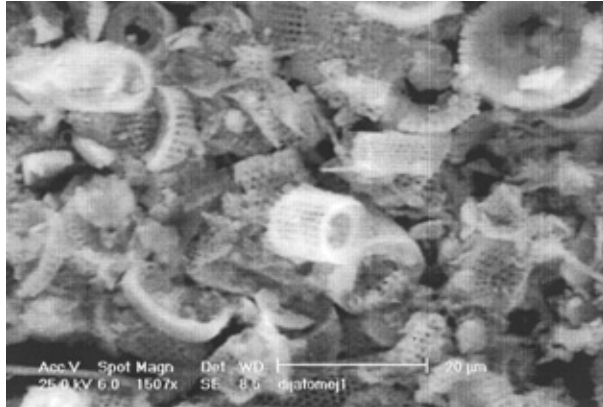


Fig. 1. SEM Image of the as-received diatomaceous earth.

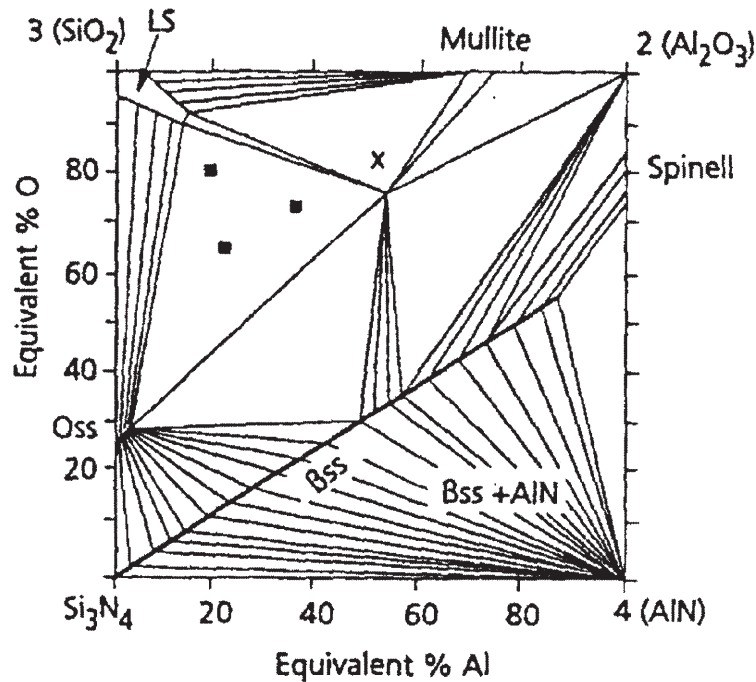


Fig. 2. The Si-Al-O-N behavior diagram based on experimental data at 1600 °C.¹ LS – Oxide nitride liquid, O – $\text{Si}_2\text{N}_2\text{O}$, X – $\text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$, Mullite – $\text{Al}_6\text{Si}_2\text{O}_{13}$, Spinell – $\text{Al}_3\text{O}_3\text{N}$.

where the A and B points belong to the Si-Al-O-N diagram. Point A is on the line $\text{SiO}_2\text{--}3\text{SiO}_2\text{:}2\text{Al}_2\text{O}_3\text{--Al}_2\text{O}_3$ and point B is in the interior of the Si-Al-O-N diagram, which can be a monophasic or multiphase zone.

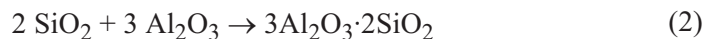
From the chemical composition of the diatomaceous earth with a constant Si/Al ratio, the line passes through a few single phase zones as well as equilibrium regions of two phases. Starting from the point on the axis $\text{SiO}_2\text{--}3\text{Al}_2\text{O}_3\text{:}2\text{SiO}_2\text{--Al}_2\text{O}_3$, the phase equilibrium line passes by the single phase zone of O-sialons, by the part with an equi-

librium of O-sialons and β -sialons, by the single phase region of β -sialons and, finally the line reaches a point where there is a mixture of Si_3N_4 and AlN (Fig. 2).

TABLE II. Phase evolution of the crystalline phases after heat treatment at various temperatures for 4 h.

Sample C/SiO ₂ mole ratio	Reaction temperature/°C	Crystalline phases
3	1200	SiO ₂ , mullite, Si ₂ N ₂ O
3	1300	SiO ₂ , mullite, Si ₂ N ₂ O
3	1400	Si ₃ N ₄ , Si ₂ N ₂ O, SiO ₂ , mullite
3	1500	Si ₃ N ₄ , SiO ₂ , mullite
4	1200	SiO ₂ , mullite, Si ₂ N ₂ O
4	1300	SiO ₂ , Si ₃ N ₄ , Si ₂ N ₂ O
4	1400	Si ₃ N ₄ , SiO ₂ , sialon
4	1500	sialon, Si ₃ N ₄ , SiO ₂
5	1200	SiO ₂ , mullite, Si ₂ N ₂ O
5	1300	SiO ₂ , Si ₃ N ₄ , Si ₂ N ₂ O
5	1400	Si ₃ N ₄ , SiO ₂ , sialon
5	1500	sialon, Si ₃ N ₄ , SiO ₂

The evolution of the crystalline phases formed as a function of the reaction temperature is shown in Table II. At the low temperature (1200 °C), there were three phases: cristobalite (SiO₂), mullite (3Al₂O₃·2SiO₂) and Si₂N₂O (sinonite). Cristobalite was the principal phase, however, this phase tends to decrease with increasing temperature. This behavior results from the formation of mullite and Si₂N₂O. Mullite is formed by recrystallization of the starting diatomaceous earth through direct reaction between SiO₂ and Al₂O₃:



Reaction (2) explains the appearance of mullite, which increased at 1300 and 1400 °C and then disappeared at 1500 °C. Since mullite originates from the recrystallization of diatomaceous, it is highly reactive in the formation of nitrogenous phases.

The formation of Si₂N₂O is based on the reaction:



which involves a vapor phase consisting of SiO and N₂ and yields powdrous Si₂N₂O. The appearance of a Si₂N₂O phase indicates that prior to reaction (3), the carbothermal-reduction of SiO₂ occurred according the reactions (4) and (5):



The XRD pattern shows a remarkable broadening of the diffraction lines in the regions around 33–34 and 35–37° 2 θ , which can be associated with the β -Si₃N₄

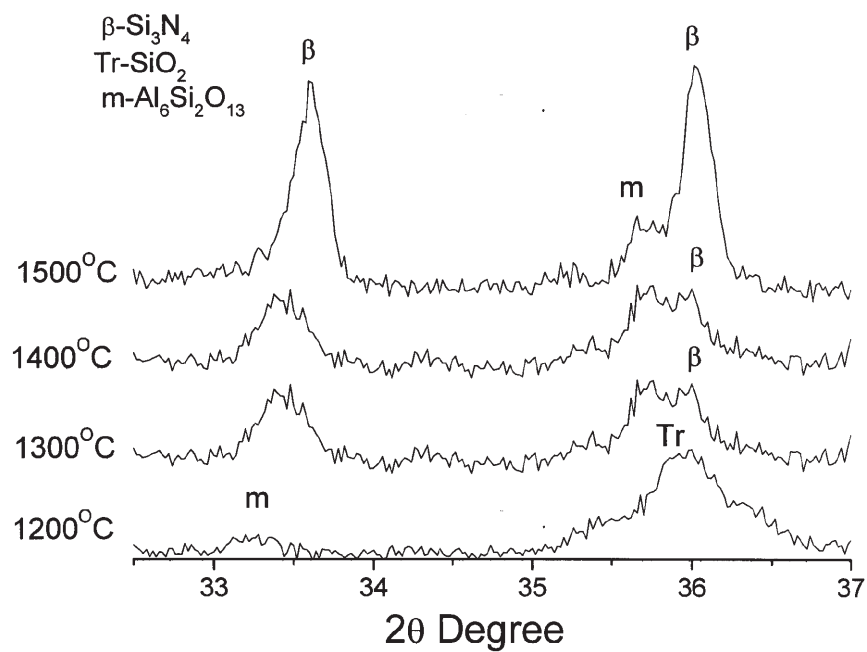


Fig. 3. XRD Patterns after different heat treatments of a 3:1 molar mixture of carbon black and silica.

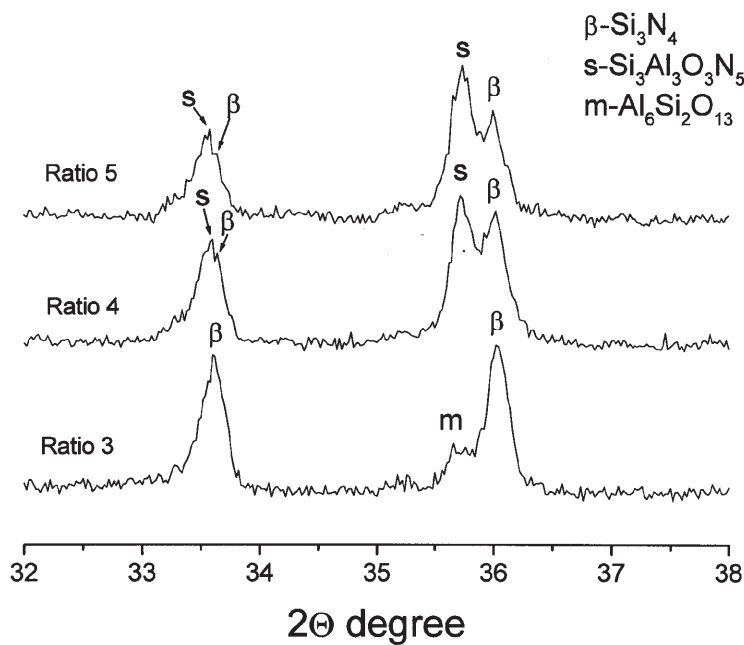


Fig. 4. XRD Patterns of the reaction products with different molar ratios of carbon black and silica, after heat treatment at 1500 °C.

phase. This indicates that nucleation and crystallization of β - Si_3N_4 occurred at 1300 °C (Fig. 3). However, with increasing C/SiO₂ ratio, β - Si_3N_4 tends to disappear with increasing temperature (Fig. 4). In samples with C/SiO₂ ratios 4 and 5, the principal phase was β' -sialon. As mention before, this coincided with the disappearance of mullite, what indicates that mullite plays a mayor role in the formation of β' -sialon. This can be explained by the reduction of mullite. The Al₂O₃ from mullite can be reduced to AlN, which is dissolved in β - Si_3N_4 according to the equation:²



where "z" represents the number of replaced Al an O ions. Increasing the C/SiO₂ ratio means that there are more contact points between C and Al₂O₃, resulting in a greater amount of reduced Al₂O₃. The total amount of dissolved AlN is higher and, as a consequence, the amount of β' -sialon is higher.

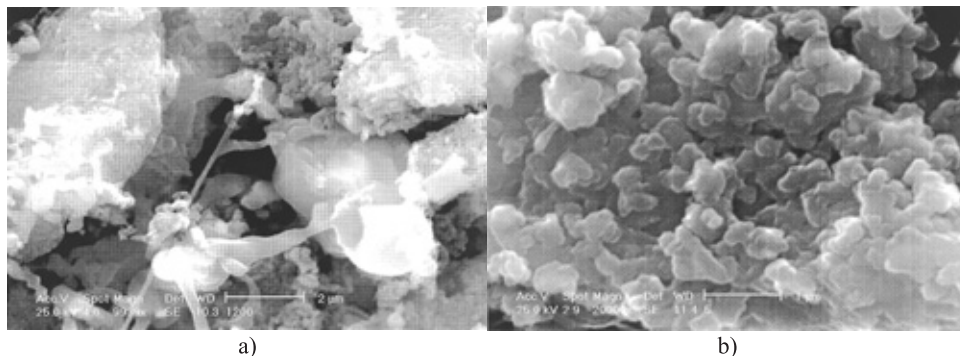


Fig. 5. SEM Micrograph of the powders obtained after 4 h at the lower temperature – 1200 °C (a) and at the higher temperature – 1500 °C (b), molar ratio (C/SiO₂) = 4.

The morphology of the powder obtained at the low temperature showed that these products retain the characteristic of some fragments of the original diatomite (Fig. 5a). However, at higher temperatures, the micrographs of the powder were completely different (Fig. 5b); these particles exhibited polygonal habitus, which is characteristic of hexagonal sialon and silicon nitride crystals.

CONCLUSIONS

The carbonitriding of diatomaceous earth leads to the formation of phases of the Si–Al–O–N system. The reaction products depend on the reaction temperature and the carbon/ silicon ratio, and many intermediate compounds appeared in small quantities. At low temperature, the reaction products are a mixture of different oxides and Si₂N₂O, with a morphology that retained some features of the starting diatomite. Powders obtained at higher temperatures were a mixture of sialon and silicon nitride, with a well-defined crystal geometry. Increasing the carbon/silicon ratio, resulted in an increased amount of sialon increase relative to silicon nitride.

Acknowledgement: The authors are grateful to the Ministry of Science and Environmental Protection of Serbia for financial support.

ИЗВОД

КАРБОТЕРМАЛНО НИТРИРАЊЕ ДИЈАТОМЕЈСКЕ ЗЕМЉЕ: ФАЗНЕ ПРОМЕНЕ И РЕАКЦИОНИ МЕХАНИЗМИ

БРАНКО МАТОВИЋ, АЛЕКСАНДРА ШАПОЊИЋ И СНЕЖАНА БОШКОВИЋ

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У раду су приказани резултати испитивања дијатомејске земље као прекурсора за синтезу неоксидних прахова на ниској температури применом карботермалног нитрирања. Утврђено је да се овим поступком добијају фазе које одговарају Si–Al–O–N систему. На 1200 °C је добијен наночестични прах. Тако ниска температура синтезе је приписана нанопорозитету стартног материјала. Развој кристалних фаза се одвија преко многих међуфаза. Прахови су окарактерисани помоћу рендгенске дифракције (XRD) и скенирајуће електронске микроскопије (SEM). Резултати су показали да дијатомејска земља представља веома погодан извор за синтезу неоксидних прахова.

(Примљено 14. јула, ревидирано 11. новембра 2005)

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