

SiC Fabrication by carbothermal reduction of sepiolite

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In this paper, the possibility of using sepiolite as Si precursor for low temperature synthesis of silicon carbide (SiC) via carbothermal-reduction reactions was studied. A sepiolite of Serbian origin and carbon (precursor-saccharose) as reducing agent were used. The green bodies with C/SiO₂ = 7 ratio were carbonised at 1073K and heat-treated at 1673K (controlled Ar flow atmosphere). Phase evolution, phase content and weight loss were followed as a function of temperature and chemical activation processes of sepiolite. Starting materials and products have been characterized by means of XRD and SEM (EDS) investigations. The results show that sepiolite can be very effective source for obtaining of silicon carbide powders.

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1. Introduction

Silicon carbide is an important structural material because of its unique combination of properties, such as high temperature strength, thermal shock resistance and resistance to wear and corrosion [1]. Thus, SiC has been a major candidate material for widespread use in engineering applications. The synthesis of pure SiC powder is one of the important factors for obtaining dense SiC ceramics [2]. Although the quality and performance are important, the cost of mass production should be the key factor in the commercialization of SiC ceramics [3]. The most promising candidate for obtaining a large variety of non-oxides products with important technical uses is carbothermal-reduction reaction (CRR) [4]. This reaction involves reduction of oxygenated materials, such as silica (SiO₂) usually by mixing with a reducing agent (carbon) in excess at the temperature higher than 1600 °C for several hours under an inert atmosphere. This liberates Si or SiO in gaseous form, which further reacts with excess carbon to form SiC following the general reaction:



Formation of final product is more complex than described by the above equation because of many intermediate stages [5]. However, CRR offers the possibility of an economically attractive production route for SiC, basing on naturally occurring materials. Many authors have studied the formation of SiC powders from the raw materials, such as high purity quartz sand [6-8] and from aluminosilicates [9]. Among the raw materials that may be used for SiC powder production, sepiolite has some advantages such as high specific surface area, high silica content and low price. Several papers were published with the similar subject, i.e. production or

sintering of Si₃N₄ powders from carbothermally reduced sepiolite [10,11].

Sepiolite is a natural occurring mineral (magnesium-silicate) with fibrous morphology, whose structure is composed of two bands of silica tetrahedrons linked by magnesium ions in octahedral coordination, thus forming open channels of fixed dimensions running parallel to the chains. 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. However, by our best knowledge, no work has yet been done on syntheses of SiC by using sepiolite as Si source.

In this paper, CRR method has been used to produce SiC powder from the cheap commercial raw material - sepiolite and carbon (saccharose) as reducing agent.

2. Experimental

A sepiolite of Serbian origin (chemical formula – Mg₄Si₆O₁₅(OH)₂6H₂O) and carbon obtained from precursor (saccharose), as a reducing agent were used for production of nanosized SiC powders. Chemical composition of as-received sepiolite: SiO₂-47.5 wt%, MgO-29.0 wt%, Al₂O₃-5.2 wt%, Fe₂O₃-1.4 wt%, CaO-1.0 wt%; rest is zeolitic and bound (constitutional) water.

Some of sepiolite powders are leached in HCl (0.1M, 0.5M, 1M) for 72h, filtered, washed with H₂O, dried (383K, 1h), and weight measured before mixing with sugar solution. C/SiO₂ ratio is calculated in respect of carbon residue at 1073K (C/SiO₂=7). Sepiolite/carbon samples are prepared by following procedure: saccharose (2.2g) is previously dissolved in water (50ml) and then mixed with sepiolite powder (1g, dried at 383K, 2h). Excess liquid is removed by gentle heating. Samples were then carbonized up to 1073K (2K/min, Ar) and heat-treated at 1673K (1h) in Ar flow atmosphere. The argon flow was kept during cooling until 300K.

Structural analysis of powdered samples was carried out by a Siemens D-500 powder diffractometer. $\text{CuK}\alpha$ radiation was used in conjunction with a $\text{CuK}\beta$ nickel filter. The average crystallite size, $\langle D \rangle$, was calculated from Scherrer's formula. The microstructural study and energy dispersive analysis of X-rays (EDS), were performed on samples with Au coating with JEOL 6300F scanning electron microscope (SEM).

3. Results and discussion

Firstly, we examined influence of acid and temperature treatment on sepiolite samples without carbon additions. XRD patterns (taken at 298K) of acid treated sepiolite samples are presented in Fig. 1. Intensities of sepiolite reflections (JCPDS number 26-1226) decreased with increasing acid concentration (Fig. 1a-d), but original sepiolite structure is still preserved. Only when undiluted (12M) HCl is used (Fig. 1e), sepiolite disintegrates completely into the amorphous SiO_2 ($2\theta \approx 21.8^\circ$) and quartz ($2\theta = 26.6^\circ$, JCPDS number 33-1161). Weight loss due to acid leaching increase from 18 to 39wt% respectively to acid concentration. XRD patterns of filtrates shows presence of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, reflections intensities increased with increasing acid concentration. This indicated that Mg-ions are leached away from sepiolite by acid attack, thus decreasing Mg content in sepiolite.

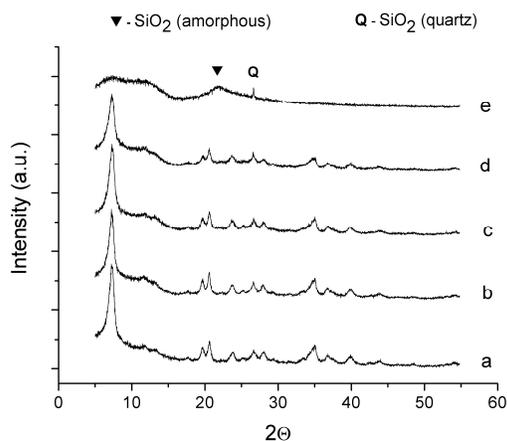


Fig. 1. XRD patterns of acid treated sepiolite samples: a) no acid, b) 0.1M HCl, c) 0.5M HCl, d) 1M HCl, e) undiluted HCl.

XRD patterns of as-received sepiolite heat-treated at different temperatures are given in Fig. 2. With increasing the temperature, sepiolite structure is deteriorated and at 1073K (Fig. 2d) amorphous material is obtained, similar to that obtained by leaching with 12M HCl (Fig. 1e). At 1273K (Fig. 2e) reflections belonging to enstatite appears

(MgSiO_3 , JCPDS number 11-0273), becoming more pronounced when temperature increased toward 1673K (Fig. 2f-i). Intensity of peak positioned at $2\theta = 21.8^\circ$, is stronger than it should be (when comparing with database spectra of various enstatites), indicating possible presence of cristobalite (SiO_2 , JCPDS number 11-0695) which strongest line is also positioned at $2\theta = 21.8^\circ$.

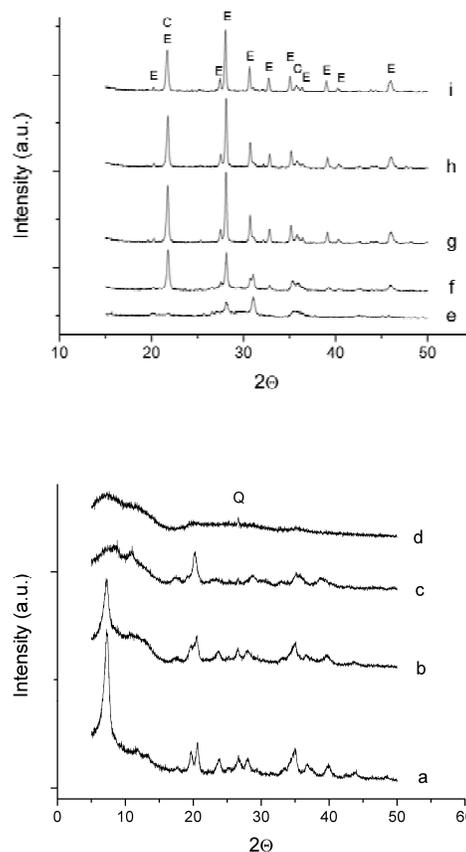


Fig. 2. XRD patterns of heat treated sepiolite: a) 293K, b) 673K, c) 873K, d) 1073K, e) 1273K, f) 1373K, g) 1473K, h) 1573K, i) 1673K, (E – enstatite, C – cristobalite, Q – quartz).

XRD patterns of acid leached samples after heat treatment at 1673K are shown in Fig. 3. As one can see, enstatite content in samples decrease with increasing acid concentration. This is in accordance with previously observed weight loss of acid treated samples: higher acid concentration \rightarrow smaller Mg content \rightarrow less MgSiO_3 is formed. Beside that, most important observation is that reflection positioned at 21.8° became stronger with increasing acid concentration, thus confirming that cristobalite is formed in greater amount in samples treated with higher acid concentrations, i.e. in samples with smaller Mg content.

XRD patterns of sepiolite/carbon samples heat treated at 1673K are given in Fig. 4. SiC is identified in all samples as β -form (JCPDS number 29-1129). Forsterite (Mg_2SiO_4 , 34-0189), suessite (Fe_3Si , 35-0519) are also

identified in some samples. Relative-intensities ratio of SiC to forsterite ($I_R = I_{\text{SiC}}/I_{\text{Mg}_2\text{SiO}_4}$) increase with increasing acid concentration.

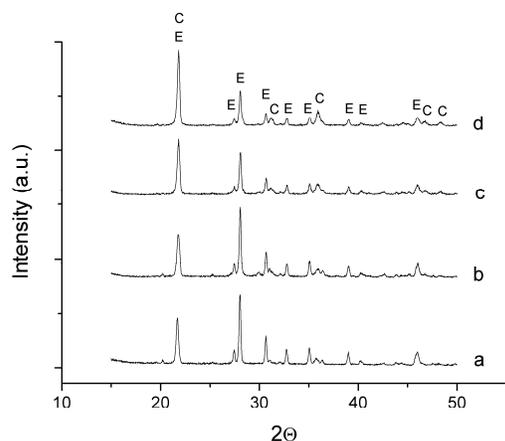


Fig. 3. XRD patterns of acid leached samples after 1673K treatment: a) no acid, b) 0.1M HCl, c) 0.5M HCl, d) 1M HCl, (E – enstatite, C – cristobalite).

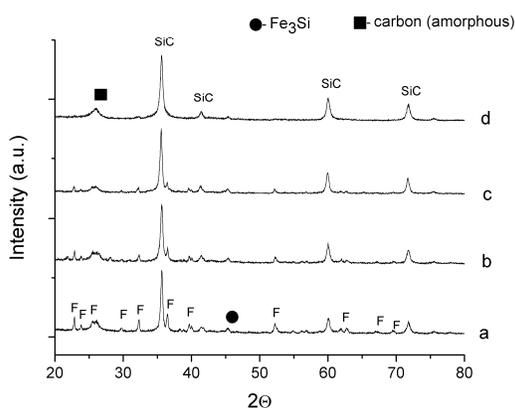
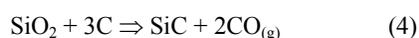
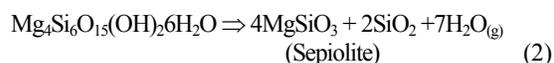


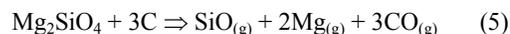
Fig. 4. XRD patterns of sepiolite/carbon samples after 1673K treatment: a) no acid, b) 0.1M HCl, c) 0.5M HCl, d) 1M HCl, (F – forsterite).

Calculated average crystallite size for SiC in all samples varying from 22nm (Fig. 4d) to 27 nm (Fig. 4a).

When pure sepiolite is heated up to 1673K, enstatite is formed together with cristobalite (SiO_2) as was observed before [10]. Obviously, forsterite formation is linked with presence of carbon and these processes can be described by considering the following steps:



Absence of forsterite and/or any other magnesium-related oxide in SiC sample shown in Fig. 4d, can be explained by forsterite reduction in a presence of excess carbon [10]:



Thus, magnesium was evaporated together with CO and swept away by the argon flow. Gaseous SiO may react with carbon and produce SiC [5]. Also, when analyzing results shown in Fig. 4, we should bear in mind what we observed earlier: higher acid concentration \rightarrow smaller MgSiO_3 content (less Mg_2SiO_4 formed) \rightarrow more SiO_2 formed, and thus, more SiC.

Obviously, sample with highest cristobalite (SiO_2) content (Fig. 4d) gives high purity SiC, whilst others contain small amounts of forsterite and Fe_3Si .

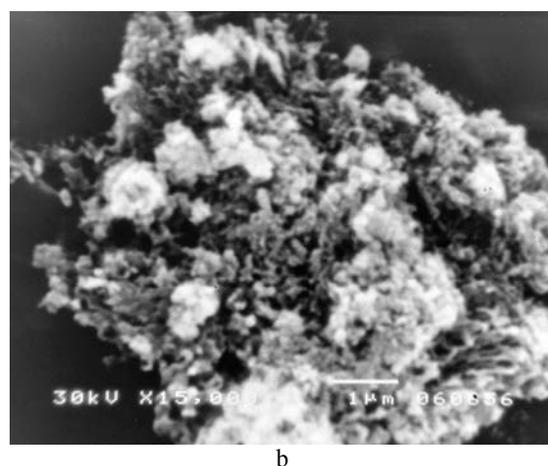
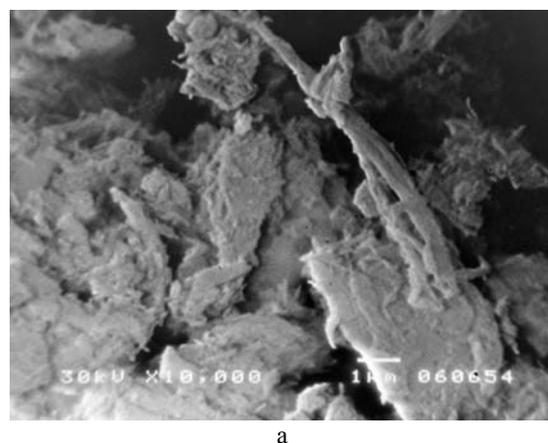


Fig. 5. SEM micrographs of: a) sepiolite leached in 1M HCl, b) SiC obtained from the same (Fig. 4d).

SEM micrographs of sepiolite sample leached in 1M HCl, and SiC obtained from the same (after removal of free carbon at 873K, air, 2h) are presented in Fig. 5. As one can see, fibrous morphology of sepiolite (Fig. 5a) is not preserved in obtained SiC powder (Fig. 5b), which

consisted from agglomerates of very fine particles (average particle size < 100nm). EDS spectra (Fig. 6) shows strong presence of Si, with no traces of oxygen, magnesium or iron, as already observed with XRD analysis. Carbon presence cannot be confirmed because of instrument limitations. However, absence of oxygen in EDS spectra, together with XRD pattern of this sample suggest that this is very pure SiC phase.

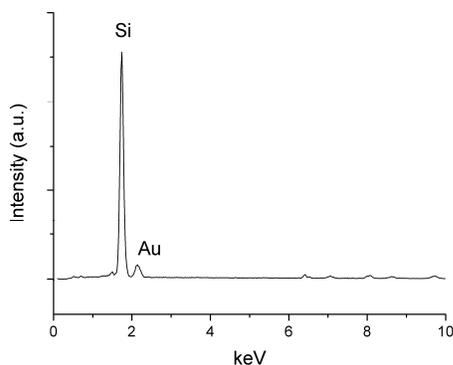


Fig. 6. EDS spectra of the SiC shown in Fig. 5b.

4. Conclusions

According to the presented results, pure silicon carbide was obtained by carbothermal-reduction reactions when saccharose (as carbon precursor) and acid treated sepiolite (as a precursor of Si) were used. Good quality SiC is obtained at rather mild conditions (1673K, 1h) when compared with literature data ($T=1773-2273K$) [8]. Obtained SiC consists of agglomerates of very fine particles with an average particle size below 100 nm, as observed by SEM.

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