



SiC synthesis using domestic mineral resources

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Abstract

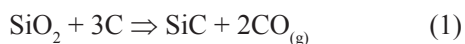
The possibility of using domestic Mg-silicate (sepiolite, white) as Si source and novolac resin (as carbon source), for synthesis of fine β -SiC powder at relatively low temperatures (1673–1873 K), was demonstrated. Obtained SiC powders consist of fine β -SiC particles and did not retain the fibrous morphology of starting sepiolites. Carbothermal reduction process, which was used in this study, is greatly influenced by catalyst addition (FeCl_3 , FeSi). In order to obtain pure SiC powders, it is necessary to completely remove all Mg-species, and catalytic influence of Fe is attributed to FeSi important role in reduction of Mg_2SiO_4 and MgO into $\text{Mg}_{(g)}$. Formation of SiC whiskers is observed only in samples with Fe introduced in form of iron-silicide (FeSi).

Keywords: SiC; sepiolite; carbothermal reduction; Mg-silicate

I. 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 in 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. The most promising technique for obtaining variety of non-oxides products with important technical uses is carbothermal-reduction reaction (CRR) [3,4]. This reaction involves reduction of oxygenated materials (for example silica - SiO_2) with reducing agent (carbon) under an inert atmosphere, at the temperatures usually higher than 1873 K.

This liberates Si or SiO in gaseous form, which further reacts with excess carbon to form SiC following the general reaction [5,6]:



Formation of the final product is more complex than described by the above equation because of many intermediate stages [5,6].

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 [5,7,8]. 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 Si_3N_4 powders from carbothermally reduced sepiolite [9,10].

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 [11]. Such a high surface area is beneficial for the synthesis of SiC powder by carbothermal-reduction reaction (CRR), especially when reducing agent is introduced via liquid solution. However, by our best knowledge, no work has yet been done on syntheses of SiC by using sepiolite or other Mg-silicates as Si source.

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In this paper, CRR method has been used to produce SiC powder from the sepiolite (as Si source) and novolac resin (as carbon source).

II. Experimental

A sepiolite of Serbian origin (chemical formula: $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \times 6\text{H}_2\text{O}$) and carbon obtained from novolac resin (“Bakelite”, 6109FP), were used for production of nanosized SiC powders. Chemical composition of as-received sepiolite is presented in Table 1. Since sepiolite is firstly dried at 383 K (in order to remove any traces of moisture), weight loss at 1073 K correspond to the H_2O present in sepiolite structure.

Table 1. Chemical composition of sepiolite

Sepiolite	SiO_2	Al_2O_3	Fe_2O_3	MgO	Loss at 1073 K
[wt.%]	50.22	-	0.01	27.17	22.6

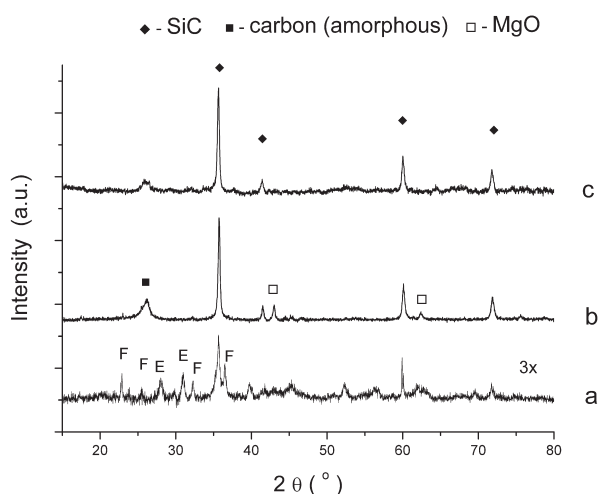


Figure 1. XRD patterns of sepiolite/novolac samples heat treated at: a) 1673K (intensity 3 times magnified for clarity), b) 1773K and c) 1873 K (F-forsterite; E-enstatite)

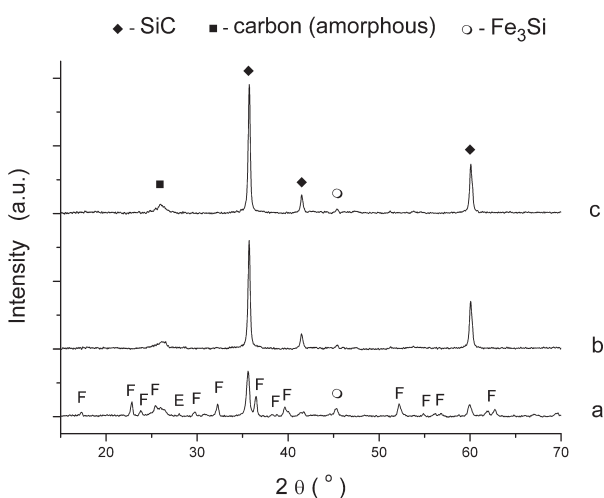


Figure 2. XRD patterns of sepiolite/Fe/novolac samples heat treated at: a) 1673K, b) 1773K and c) 1873K (F-forsterite; E-enstatite)

C/SiO_2 molar ratio in samples was calculated in respect to carbon residue at 1073 K ($\text{C}/\text{SiO}_2 = 7$). Sepiolite/carbon samples were prepared by following procedure: appropriate amounts (≈ 2 g) of novolac are dissolved in ethanol (50 ml) and then mixed with previously dried sepiolite powder (≈ 1 g, 383 K, 2 h). Excess liquid was removed by gentle heating at 333 K. Polymerization of the samples was conducted by slowly raising the temperature to 453 K in several steps. The samples were then carbonized up to 1073 K in carbonization furnace (2 K/min, Ar flow atmosphere) and then heat-treated at 1673–1873 K in “Astro” graphite furnace (1 h, Ar flow atmosphere). The argon flow was kept during cooling until 300 K.

In order to examine the catalytic influence of Fe on CRR process, 2 wt.% of Fe is added into some samples:

- by mixing the as-received sepiolite with $\text{FeCl}_3/\text{H}_2\text{O}$ solution, drying it at 383 K, and then heating it at 1073 K in air in order to decompose/oxydize FeCl_3 into the Fe-oxides. Thus obtained sepiolite was light-brown in colour, similar to the colour of the sepiolites naturally containing Fe. After that, sepiolite was mixed with novolac solution and further treated as described above.
- by mixing the carbonized sepiolite/novolac sample with FeSi powder.

Structural analysis of powdered samples was carried out by Siemens D-500 powder diffractometer. $\text{CuK}\alpha$ radiation was used in conjunction with a $\text{CuK}\beta$ nickel filter. We did not remove the free carbon before recording XRD patterns, because the appearance of amorphous carbon in XRD patterns is clear proof that 7 : 1 (C : Si) ratio is an excess of carbon, which is beneficial in suppressing some undesired reactions in $\text{SiO}_2/\text{C}/\text{SiC}$ system [5].

The microstructural study and energy dispersive analysis of X-rays (EDS) were performed on samples with Au coating with VEGA TS 5130 mm, TESCAN scanning electron microscope (SEM). Prior to SEM/EDS analysis, samples were oxidized in air at 873 K (2 h), in order to remove the residual (unreacted) carbon which, if not removed, makes SEM/EDS analysis rather difficult.

Chemical composition of sepiolite is obtained by XRF analysis, Axios – PANalytical.

III. Results and discussion

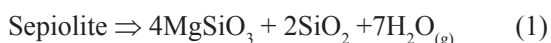
Phases identified from XRD patterns (Figs. 1-3) of sepiolite/carbon samples heat-treated at 1573–1873 K are given in Table 2. SiC is identified in all samples as β -form (JCPDS number 29-1129). Forsterite (Mg_2SiO_4 , 34-0189), Enstatite (MgSiO_3 , JCPDS number 11-0273), Periclase (MgO, JCPDS number 43-1022) and Suessite (Fe_3Si , JCPDS number 35-0519) are also identified in some samples.

Table 2. Phase composition of samples heat-treated at different temperatures

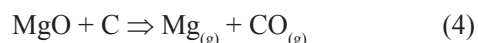
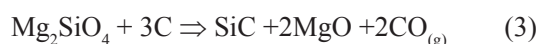
Sample	1673 K	1773 K	1873 K
Sepiolite+ novolac	SiC, F, E	SiC, MgO	SiC
Sepiolite+ Fe + novolac	SiC, F, E, S	SiC, S	SiC, S
Sepiolite+ FeSi + novolac	SiC, S	SiC, S	SiC, S

E-enstatite; F-forsterite; S-suessite

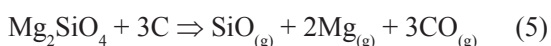
When pure sepiolite is heated up to 1673K, enstatite (MgSiO_3) is formed together with cristobalite (SiO_2) as was observed before [9]. Obviously, forsterite (Mg_2SiO_4) formation, as observed from XRD patterns in Figs. 1a and 2a, is linked with presence of carbon and these processes can be described by considering the following steps:



Reduction of forsterite into the MgO and latter disappearance of MgO with temperature increase, as observed from XRD patterns of samples prepared without Fe addition (Fig. 1), can be described by two-step reduction:



Disappearance of forsterite without MgO formation, as observed in XRD patterns of samples prepared with Fe (Table 2, Figs. 2 and 3), can be explained by forsterite reduction in presence of an excess of carbon, as proposed by Kurt and Davies [10]:



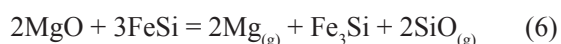
According to this, Mg was evaporated together with CO and swept away by the argon flow. Gaseous SiO

may react with carbon and produce SiC or also be swept away by argon flow.

However, question is *why* the reaction (5) is not occurring in samples with same C/Si ratio, but *without Fe addition*, where excess carbon is also presented (Fig. 1).

We offer another explanation for disappearance of forsterite without MgO formation, which is based on fact that *formation of Fe_3Si* is observed in *all samples containing Fe* (Table 2, Figs. 2 and 3).

Since it is well known that iron-silicides are commercially used for $\text{MgO} \rightarrow \text{Mg}_{(g)}$ reduction [12], Fe_3Si formation in samples where Fe is added through FeSi powder, can be explained by following reaction:



If reaction (6) is much faster than reaction (3), all MgO produced will be instantly transformed into the $\text{Mg}_{(g)}$. Also, we cannot exclude the possibility that FeSi may react with the forsterite in a way similar to that described by reaction (5), i.e. by producing gaseous SiO and Mg directly from forsterite.

Since we know that the formation of Fe and FeSi in systems similar to ours is thermodynamically possible at 573–1073 K [12–14], and since Fe_3Si formation is observed in all samples prepared with FeCl_3 (Table 2, Fig. 2), it is quite logical to assume that FeSi is also formed in these samples and then reduced into the Fe_3Si as presented by reaction (6).

However, method of introducing the Fe into the samples by $\text{FeCl}_3/\text{H}_2\text{O}$ solution is not as effective as method where Fe is introduced by addition of FeSi powder. As one can see from Table 2, the first method gives pure SiC phase at 1773 K, whilst the second method gives pure SiC phase at 1673 K. We use term “pure SiC phase”, because Fe_3Si phase can be easily removed by leaching in acids, whilst residual (free) carbon is easily removed by oxidation in air [15]. It is also obvious that more Fe_3Si phase is formed in sample prepared with FeSi powder (Fig. 3a) than in sample prepared with $\text{FeCl}_3/\text{H}_2\text{O}$ solution (Fig. 3b).

Results of SEM/EDS analysis of samples prepared with Fe addition are shown in Figs. 4 and 5. As one can see, by using BSE (Back Scattering Electrons) detector mode, Fe-containing particles became clearly visible, usually as brightly white spheres with $\approx 1 \mu$ in diameter. Since they are smaller than beam focus ($\approx 5 \mu$), their EDS analysis is rather difficult. High O content is probably due to oxygen bonded to Fe_3Si phase. This is

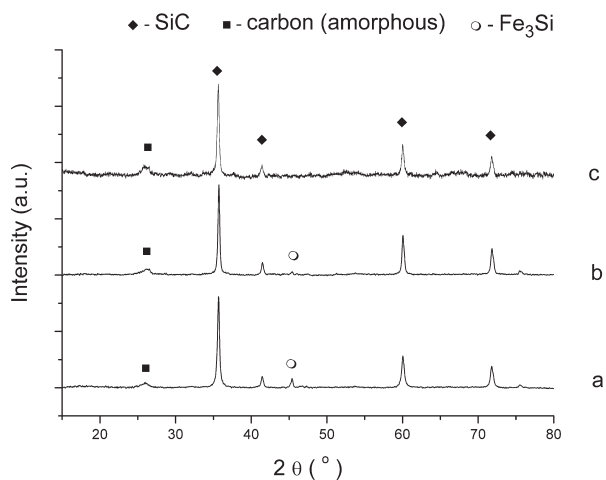
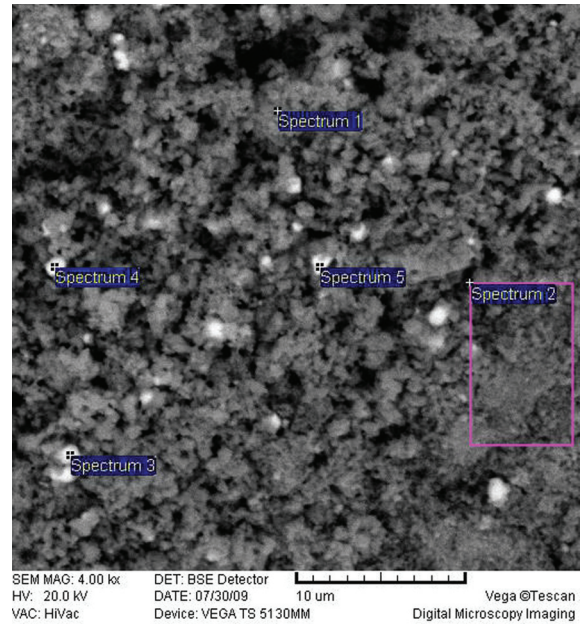
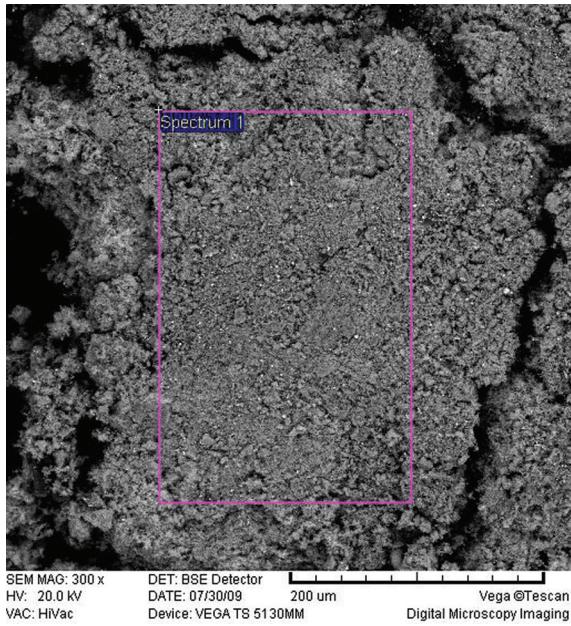


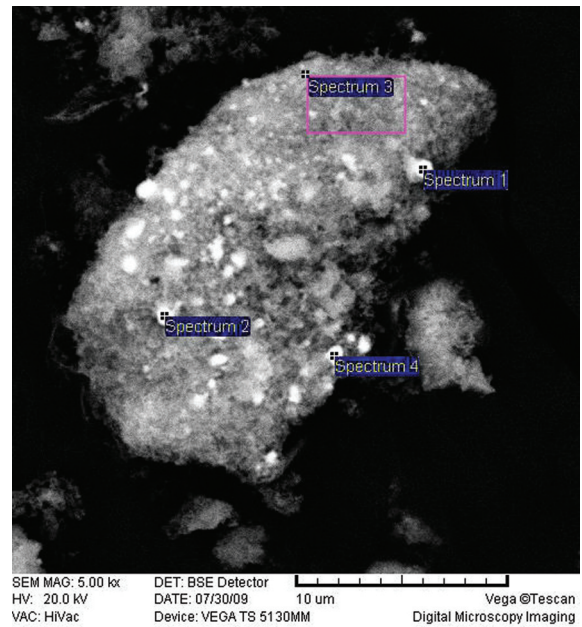
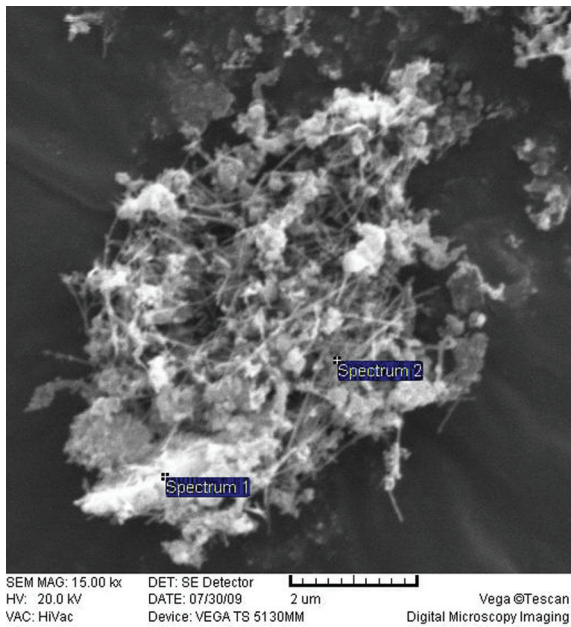
Figure 3. XRD patterns of samples containing only SiC phase: a) sepiolite/novolac/FeSi at 1673 K, b) sepiolite/novolac/Fe at 1773K and c) sepiolite/novolac at 1873K



Composition [wt.%]	O	Si	Fe
Spectrum 1	5.31	88.43	6.26

Composition [wt.%]	O	Si	Fe
Spectrum 1	3.99	93.74	2.27
Spectrum 2	6.21	88.59	5.20
Spectrum 3	8.06	41.59	50.06
Spectrum 4	5.61	44.08	49.78
Spectrum 5	4.10	66.57	28.75

Figure 4. SEM/EDS analysis of sepiolite/Fe/novolac sample heat treated at 1773K



Composition [wt.%]	O	Si
Spectrum 1	13.91	86.09
Spectrum 2	10.56	89.44

Composition [wt.%]	O	Si	Fe
Spectrum 1	20.26	31.34	48.40
Spectrum 2	14.64	52.78	32.58
Spectrum 3	11.48	83.30	5.22
Spectrum 4	21.25	57.17	21.58

Figure 5. SEM/EDS analysis of sepiolite/FeSi/novolac sample heat treated at 1673 K

not surprising, since iron-silicides are commonly used in metallurgy as “sponge” for removal of oxygen from system [12]. Pure SiC phase appears in SEM images as grey porous surface, which consisted from agglomerates of very fine particles, which is very similar to SiC phase obtained by carbothermal reduction of another fibrous magnesium silicate (mountain leather asbestos) [15].

Another difference between samples prepared with $\text{FeCl}_3/\text{H}_2\text{O}$ solution and FeSi powder, can also be observed from SEM images shown in Figs. 4 and 5: SiC whiskers are formed only in the sample prepared with FeSi powder. This indicates that amount of FeSi formed in the sample prepared with $\text{FeCl}_3/\text{H}_2\text{O}$ addition is obviously not big enough to produce SiC whiskers, which grows easily from FeSi melt [16–18] by well known VLS (Vapour-Liquid-Solid) mechanism.

IV. Conclusions

According to the presented results, pure silicon carbide can be obtained by carbothermal reduction of domestic mineral resource (sepiolite) at rather mild conditions (1673–1873K). It was shown that both the presence of Fe in system and method of introducing it, are important factors that can significantly influence the final temperature needed for complete carbothermal reduction of sepiolite into the SiC. Pure SiC samples are obtained after the complete removal of Mg-containing species. Introducing the Fe by addition of the FeSi powder seems to be the most effective way when regarding the final temperature needed for obtaining the pure SiC phase, and in addition to the main phase which consists of agglomerates of very fine SiC particles, it also produce SiC whiskers.

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References

1. M.M. Schwartz, *Handbook of structural ceramics*, McGraw-Hill, 1992.
2. K. Komeya, pp. 175–223 in *Fine Ceramics*. Ed. S. Saito, Elsevier Science Publishing Co., New York, 1988.
3. G. Petzow, M. Herrmann, pp. 47–167 in *Structure and Bonding*, Vol. 102. Ed. M. Jansen, Springer-Verlag, Berlin, 2002.
4. V. Hlavacek, J.A. Puszynski, “Chemical engineering aspects of advanced ceramic materials”, *Ind. Eng. Chem. Res.*, **35** [2] (1996) 349–377.
5. V.D. Krstić, “Production of fine, high-purity beta silicon carbide powders”, *J. Am. Ceram. Soc.*, **75** [1] (1992) 170–174.
6. D.H. Filsinger, D.B. Bourrie, “Silica to silicon: Key carbothermic reactions and kinetics”, *J. Am. Ceram. Soc.*, **73** [6] (1990) 1726–1732.
7. W. Schwetz, H. Lipp, p. 479 in *Herstellung und Eigenschaften ultrafeiner beta-SiC Sinterpulver*, Heft 2, Radex-Rundschau, 1978.
8. A.K. Schwetz, p. 26 in *Silicon Carbide and its High-technology Ceramics*, Heft 1, Radex-Rundschau, 1989.
9. Y. Sugahara, K. Kuroda, C. Kato, “Nitridation of sepiolite by carbothermal reduction”, *J. Mater. Sci. Lett.*, **4** [7] (1985) 928–931.
10. A.O. Kurt, T.J. Davies, “Pressureless sintering of Si_3N_4 powders obtained from carbothermally reduced sepiolite”, *J. Mater. Sci. Lett.*, **20** [11] (2001) 1067–1070.
11. C. Pecharroman, A. Esteban-Cubillo, I. Montero, J.S. Moya, E. Aguilar, J. Santaren, A. Alvarez, *J. Am. Ceram. Soc.*, **89** [10] (2006) 3043–3049.
12. C.K. Gupta, *Chemical metallurgy*, Wiley-VCH, Weinheim, 2003.
13. Y. Zhang, “Interfacial reactions in thin film and bulk iron/silicon diffusion couples”, *Master of Science thesis*, Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada, 1997.
14. I. Filipović, S. Lipanović, *Opća i anorganska kemija*, Školska Knjiga, Zagreb, 1987.
15. A. Devečerski, M. Pošarac, A. Egelja, A. Radosavljević-Mihajlović, S. Bošković, M. Logar, B. Matović, “Fabrication of SiC by carbothermal-reduction reactions of mountain leather asbestos”, *J. Alloys Compd.*, **464** [1-2] (2008) 270–276.
16. Y.-J. Lin, C.-M. Chuang, “The effects of transition metals on carbothermal synthesis of β -SiC powder”, *Ceram. Int.*, **33** [5] (2007) 779–784.
17. B.-H. Yoon, C.-S. Park, H.-E. Kim, Y.-H. Koh, “In situ synthesis of porous silicon carbide (SiC) ceramics decorated with SiC nanowires”, *J. Am. Ceram. Soc.*, **90** [12] (2007) 3759–3766.
18. G. Yang, R. Wu, J. Chen, F. Song, Y. Pan, “Growth of silicon carbide whiskers in Fe_xSi_y flux”, *Mater. Chem. Phys.*, **106** [2-3] (2007) 236–239.