Synthesis of SiC nanofibers via carbothermal method using different carbon sources

M. Taghavi[a], E. Ghasemi[b,*] and A. Monshi[c]

[a]*Islamic Azad University of Najafabad, Najafabad, Iran*
[b]*Institute for Color Science and Technology, 1668814811 Tehran, Iran*
[c]*Isfahan University of Technology, Department of Materials Science, Isfahan, Iran*

In this research, the effect of milling time and carbon sources was investigated on the β-SiC nanofiber formation via the carbothermal process. Carbon black and petroleum coke were used as carbon sources. They were mixed with microsilica separately; milled for different periods of time and fired at 1450 ºC. Phase formation and microstructure of samples were studied using X-ray powder diffraction and scanning electron microscopy, respectively. The results indicated that milling process for 5 h appreciably contributes to the formation of β-SiC phase. Moreover, it was revealed that the carbon black leads to formation of fiber-like SiC nonaparticles.

Key words: Carbothermal, Mechanical alloying, SiC, Nano-fiber.

Introduction

Silicon carbide (SiC) fibers are applied for reinforcement of metal based, ceramic based and polymer based composites due to its excellent mechanical, thermal and chemical properties such as low thermal expansion, high module of elasticity, refractoriness, low density and high oxidation resistance [1]. The composite properties are more improved when SiC particles are in nanoscale range or the morphology is fiber-like [2].

Short SiC fibers can be produced from various processes such as direct carbonization of silicon, chemical vapor deposition, sol-gel, carbothermal reaction and mechanical alloying. Mixing of carbothermal reduction with vapor-liquid-solid (VLS) mechanism is the most applicable method for synthesis of these fibers [2, 3].

The general reaction for SiC formation in carbothermal method is:

$$SiO_{2(s)} + 3C_{(s)} = SiC_{(s)} + 2Co_{(g)} \tag{1}$$

This reaction is intensively endothermic and its enthalpy is $\Delta H = 618.5$ KJ.

The industrial production of SiC mainly is performed via Acheson method. The problem of this method is its high temperature and long time which lead to the production of large particles; however, due to the low price needed for the raw materials in this method, carbothermal is still considered as one of the main methods for production of SiC [4].

Sanjay Dhage et al. [5] produced SiC powder with crystallite size of less than 150 nm via carbothermal method using silica and active carbon as raw materials. Eskandarany et al. [6] produced SiC powder via solid state reaction of Si and carbon powder using mechanical alloying at room temperature. They have reported SiC with cubic structure after 300 h of milling.

Guo et al. [7] used mechanical alloying to produce SiC powder. They have reported the crystallite size of 70 nm for SiC particles via scherrer formula. Similar methods was used by Ghosh et al. [8]. They have reported the average crystallite size of 40-70 nm for produced SiC particles after 15 h milling time.

Although SiC fibers are widely produced via carbothermal method or reaction of hydrogen Polycarbosilaneon carbon substrate, the VLS mechanism is more common for the production of SiC fibers and whiskers [9].

In this research we have used carbothermal method for production of SiC nanofibers. The effects of different carbon sources and mechanical alloying process on formation of these fibers are also addressed in this work.

Materials and Methods

Petroleum coke and Carbon black separately were mixed with microsilica using a mechanical mixer at the ratio of 3 : 1. The details of raw materials can be seen in Table 1. The Carbon Black containing sample was marked as S1 and the petroleum coke containing sample as S2 in all research process.

To study the milling effect a planetary mill was used with stainless steel balls and cup. The mixed powders were transferred to it and milled with speed of 600 r.p.m for times of 0, 5, 10 and 15 h under a

*Corresponding author:
Tel : +98-2122951484
Fax: +98-2122939557
E-mail: eghasemi@iust.ac.ir

Table 1. Raw materials specifications.

Starting materials	SiO	C	FeO	Al$_2$O$_3$	CaO	S	Size
Microsilica	95	0.6	1.2	1.2	1.5	0.08	> 1 μm
Petroleum coke	–	98	–	–	–	–	> 0.15 μm
Carbon Black	–	99	–	–	–	0.19	> 100 nm

protecting atmosphere of Ar. The ratio of ball to powder was 14 : 1. After milling, the powders were pressed to cylindrical specimens of 13 mm diameter and 8 mm height using a laboratory press with a pressure of 100 MPa. The prepared specimens were fired in an electrical furnace at 1450 °C for 3 h. The purity of used Ar gas was 99.99%.

X-ray powder diffraction (XRD) measurements were carried out with Philips X. Pert using Cu-Kα radiation. The size of crystallites was calculated using Scherrer formula with some corrections. The Scherrer formula is:

$$D = 0.94\lambda \ / \ \beta Cos\theta \qquad (2)$$

Where, D is the average crystalline size, l the X-ray wavelength, β is the angular line width of the half-maximum intensity and θ is the Bragg angle in degrees. Equation (2) can be written as:

$$Ln\beta = Ln \ (0.94\lambda \ / \ D) + Ln \ (1/cos \ \theta) \qquad (3)$$

β was calculated for all peaks then the variation of lnb with ln (1/Cosθ) was drawn. The linear trend from these points was considered and its intercept which is equal to Ln (0.94λ/D) was calculated. Then the value of D calculated from equation (3).

Results and Discussion

Figs. 1 and 2 show the XRD results for S1 and S2 samples, respectively. As it is obvious in both figures, β-SiC is the prime phase after milling which corresponds to the JCPDC card no. of 29-1121.

The differences in phase formation of samples before and after milling are clear in both Figures. Fig. 1 shows that the main phases before milling are cristobalite and β-SiC whereas in Fig. 2 the main phases before milling consist of cristobalite, β-SiC and tridymite. SiC and Fe$_5$Si$_3$ are the main phases after milling for both samples. This reveals that the milling process contributes to the formation and crystallization of SiC. For sample S2 the carbon representative peak is obvious at 26.5 degree which disappears after 15 h milling. Similarly some researchers [8] have reported that after 15 h milling, the crystalline carbon might develop to amorphous phase. XRD representative peaks of Fe$_5$Si$_3$ can be attributed to impurity of iron introduced during milling. Fig. 3 shows the effect of milling time on the raw petroleum coke. After 15 h the peak of carbon has been slightly
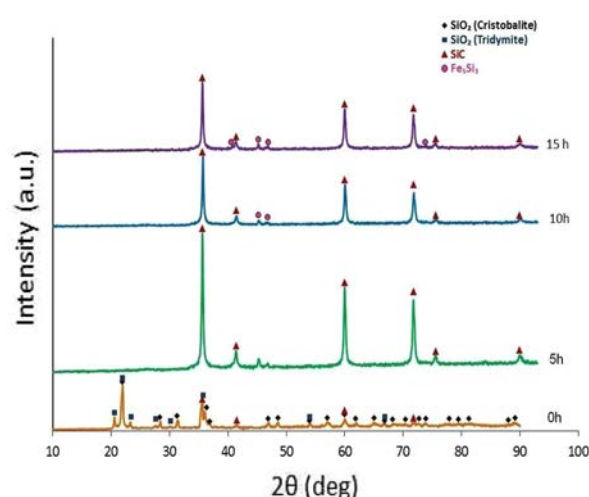
Fig. 1. XRD results for S1 after firing at 1450 °C.
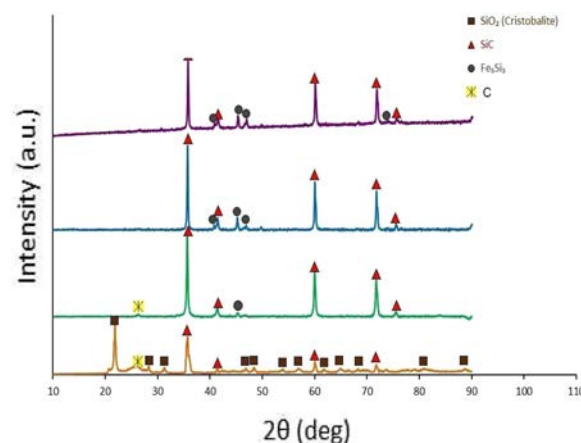
Fig. 2. XRD results for S2 after firing at 1450 °C.
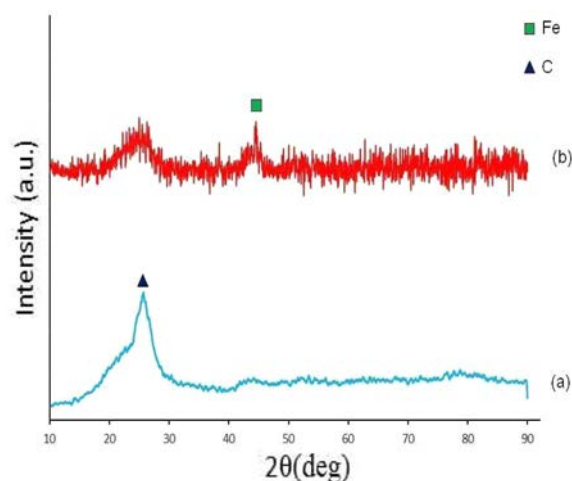
Fig. 3. XRD for petroleum coke (a) before milling, (b) after 5 h milling or petroleum coke (a) before milling, (b) after 5 h milling.

disappeared which indicates that the milling procedure leads to further amorphisation of carbon. Moreover, iron peaks can be seen in milled samples. Therefore, iron impurity is inevitable after milling and the presence of Fe$_5$Si$_3$ in fired samples is also due to iron
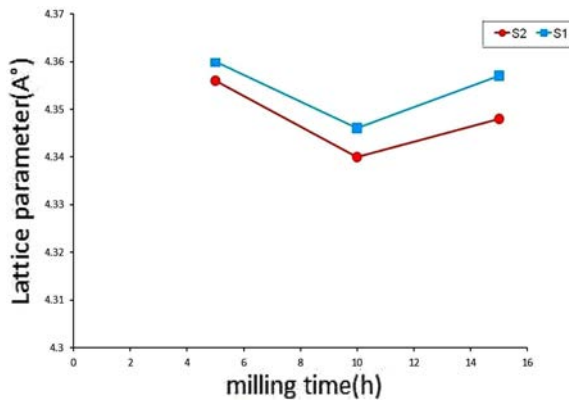
Fig. 4. variations of lattice parameter with milling time.
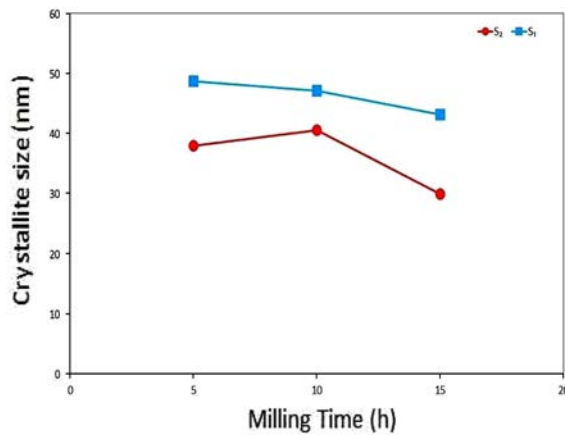

Fig. 5. crystallite size of samples of S1 and S2.

impurity.

β-SiC has a cubic structure and its lattice parameters can be calculated via the following equation:

$$a = d \big/ \sqrt{(h^2 + h^2 + l^2)} \qquad (4)$$

where a is the lattice parameter and d is the lattice plane distance. Changes in calculated lattice parameters with milling time can be seen in Fig. 4. The range of variation is from 4.338 Å to 4.358 Å.

For both samples of S1 and S2 the lattice parameter is reduced after 10 h milling and then increased after 15 h milling. Abderrazak *et al.* [10] has reported the lattice parameters of β-SiC obtained via mechanical alloying to be in the range of 4.342 Å to 4.349 Å. Referring to the value of 4.359 in JCPDS card no. of 29-1121 for β-SiC, it can be said that our results are closer to this value than theirs. This might have been resulted from firing the samples at high temperatures after milling.

The calculated crystallite sizes can be seen in Fig. 5. It is obvious that milling causes the crystallite size to reduce in both samples. Crystallite sizes are lower than 50 nm for both while for sample S2 it is lower than that for sample S1. This can be due to the difference of growing mechanisms in the two samples which will be

explained with more details in following lines. Kim *et al.* [11] has reported that the amount of SiC nanocrystals increase with increasing the carbon molar ratio. Moreover, the best ratio to achieve the smallest crystallite size is the stoichiometric ratio.

Figs. 6 and 7 show the SEM microstructures for the samples S1 and S2 after various milling times, respectively. For sample S1 (Fig. 6 a and b) no specific difference can be seen in morphologies between two milling times. Moreover there is no evidence for formation of fiber-like structures. Unlike this, in Fig. 7 noticeable differences can be seen in microstructural morphologies after each milling time. In Fig. 7a, two different spherical and fiber-like morphologies can be seen. In Fig 7b, however, the main particles are as fiber. This reveals that when the carbon source is carbon black, the formation of SiC fibers is encouraged with milling time. The mean diameter of these fibers is about 83 ± 11 nm.

A mechanism for crystal growth of β-SiC fibers and whiskers is VLS [12]. In the VLS process, V stands for vapor feed gases, L for liquid catalyst, and S for solid crystalline whisker growth. The presence of a liquid catalyst is what distinguishes this method from all other whisker growth techniques. The role of the catalyst is to form a liquid solution interface with the
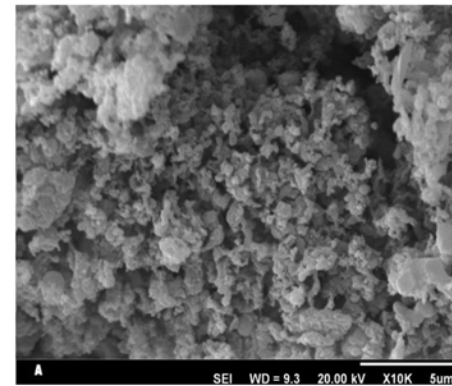
(a)
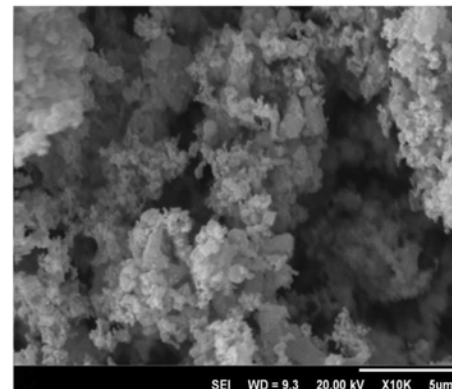
(b)

Fig. 6. SEM microstructures of Sample S2. (a) after 5 h milling (b) after 10 h milling.
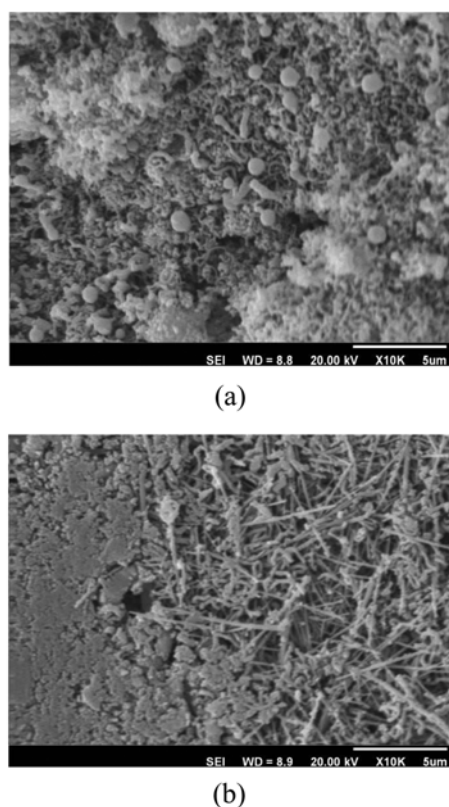
Fig. 7. –SEM microstructures of Sample S1. (a) after 5 h milling (b) after 10 h milling.

crystalline material to be grown and fed from the vapor through the liquid-vapor interface. The catalyst solution is a preferred site for deposition of feed from the vapor which causes the liquid to become supersaturated. Crystal growth occurs by precipitation from the supersaturated liquid at the solid-liquid interface. In view of this mechanism, catalyst selection is partially based upon the fact that the catalyst must display the affinity, when molten, to take into solution the constituent atoms of the whisker one which wishes to grow. For SiC whisker growth, transition metals and iron alloys satisfy this requirement. At about 1400 °C the solid catalyst particle melts and forms the liquid catalyst ball. Carbon and silicon atoms in the vapor feed are accreted to the surface by the liquid catalyst, which soon becomes supersaturated, and solid SiC precipitates from the liquid catalyst onto the growth substrate. As precipitation continues, the whisker grows, lifting the catalyst ball from the substrate and forming a whisker which is proportional in size to the catalyst ball.

It can be seen from Fig. 7(a) that some particles are in spherical forms.Moreover some fiber-like particles can be seen too. In Fig. 7(b) these balls cannot be seen,

i.e. after 10 h milling they have been disappeared and the fibers has been elongated. It can be concluded that the milling process and its time is effective for promotion of SiC fibers formation via VLS process.

As it was mentioned before, one of the effective parameters on the formation of fibers is the raw materials. From SEM studies it is well obvious that when the carbon black is used as the carbon source, the tendency to form whisker-like SiC particles is more than when petroleum is used. Presence of impurities in the coke increases the possibility for liquid phase formation at high temperatures. It is well known that the liquid phase promotes the particles to grow as spheres or disks. This is why that SiC particles are not whisker-like when the petroleum is used as the carbon source.

Conclusions

β-SiC nanofibers were synthesized using carbothermal method. The effect of carbon sources and milling time was investigated on this process. It was shown that the milling process has appreciable effects on the β-SiC phase formation, lattice parameters modifications and fibers growth. Major differences were seen in morphologies of SiC particles after firing samples with different carbon sources. It was revealed that the SiC particles are fiber-like when the carbon source is carbon black and are spherical when the carbon source is the petroleum coke. This was assigned to impurities which lead to differences in growth mechanism.

References

1. Gary L Harris , Properties of Silicon Carbide, INSPEC, the Institution of Electrical Engineer, London, United Kingdom (1995).
2. Y.F. Chen, J. Mater. Sci. Technol 26 (2010) 1041-1046.
3. H.O.Pierson, Handbook of refractory carbides and nitrides, Sandia Park, New Mexico (1996).
4. S. Larpkiattaworn, Ceramics International 32 (2006) 899-904.
5. S Dhaghe, H Lee, M Hassan, M Akhtar, C Kim, J Sohn, K Kim, H Shin, O Yang, Materials Letters 63 (2009) 174-176.
6. M.S. El-Eskandarany, Journal of Materials Research 10 (1995) 659-667.
7. Zhen-Guo Yang, Nanostructured Materials 7 (1996) 873-886.
8. B. Ghosh, S.K. Pradhan, Journal of Alloys and Compounds 486 (2009) 480-485.
9. Xiumin Yao, Ceramics International 33 (2007) 901-904.
10. H. Abderrazak, and Mohieddine Abdellaouia, Materials Letters 62 (2008) 3839-3841.
11. Sang Jin Kim, Journal of Industrial and Engineering Chemistry 16 (2010) 273-277.
12. Mats Johnsson, Solid State Ionics 172 (2004) 365-368.