THE ROLE OF SILICON DOPED CARBON POWDER ON THE FORMATION ß-SiC WHISKERS NANO SIZED DIAMETER IN SILICON-CARBON-RESOLE COMPOSITE MATERIALS

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Abstract
Silicon powders are converted into carbonized powders (silicon doped carbon) by heat treatment at 800 ºC for 1 h using phenol resole with coat-mix process. Specimens were composed of a blend of carbonized powder, carbon powder and liquid resole. They were cured at 200 ºC for 2 h and fired at three temperatures (1100 ºC , 1400 ºC and 1500 ºC) for 2 h in a coke environment to avoid oxidizing atmosphere. SEM and TEM, electron diffraction pattern (SAD), EDS analysis, XRD, STA and FTIR performed on fired samples. At 1100 ºC, nucleation of nano ß-SiC whiskers was observed but did not fully growth, since driving force isn't enough at this temperature. But, it is high enough at 1400 ºC and 1500 ºC, since the formation of SiC whiskers of nano sized diameter were completed from particles of silicon carbonized. It seems the formation is by VLS mechanism.

1 Introduction

SiC whisker is excellent in characteristics such as specific strength, specific modulus, heat resistance, chemical stability, etc. and its usefulness as a composite reinforcing material for plastics is attracting attention. The mechanical property improvements observed with the incorporation of SiC whiskers into ceramic matrices were unprecedented. For example, the fracture toughness of alumina was increased from ~3.0 MPa√m to 8.5 MPa√m with the addition of 20 v/o whiskers. This was accompanied by fracture strengths of 700-800 MPa versus 400 MPa in unreinforced alumina. Just as importantly, these property improvements were retained to elevated temperatures, unlike some other toughened ceramic systems. Remarkably improved thermal shock and creep resistance were also observed.

Several methods and numerous starting materials can be used to grow SiC whiskers. Much of the early work prior to the mid-1970s employed the vapor-liquid-solid (VLS) mechanism to produce small quantities of whiskers. Later production methods used carbothermic reduction reactions of low-cost silica and carbon precursors, such as rice hulls, to produce large quantities of whiskers at reasonable cost. This allowed SiC whiskers to become economically viable as reinforcing agents in components for large-scale, high-volume applications. Subsequent studies have examined the SiC whisker-reinforcement of numerous ceramic

matrix systems, including mullite, zirconia, glass, spinel, cordierite, silicon nitride, boron carbide, and combinations of these materials [1].

Nowadays, more and more researchers begin to utilize more than one type of reinforcing agent to fabricate ceramic matrix composites in order to improve the mechanical properties of ceramic materials to a greater degree [2]. Increasing SiC whisker content decreased the Poisson's ratio and mean coefficient of thermal expansion of the specimen and increased the elastic modulus, bend strength, and thermal diffusivity of the composites [3].

ß-SiC whiskers were synthesized by the vapor-liquid-solid (VLS) process using Fe catalyst. Whiskers show smooth surfaces and no ramifications. They have uniform diameter (0.5-1 μm) and lengths between 50 and 300 μm. A catalyst droplet was observed on the tip of almost all the whiskers. The transport of iron from the substrate surface to the SiO generators, where growth took place, occurs fundamentally via vapor phase. Fe was deposited over surfaces containing C, and whisker growth was produced where there were Fe droplets of appropriate

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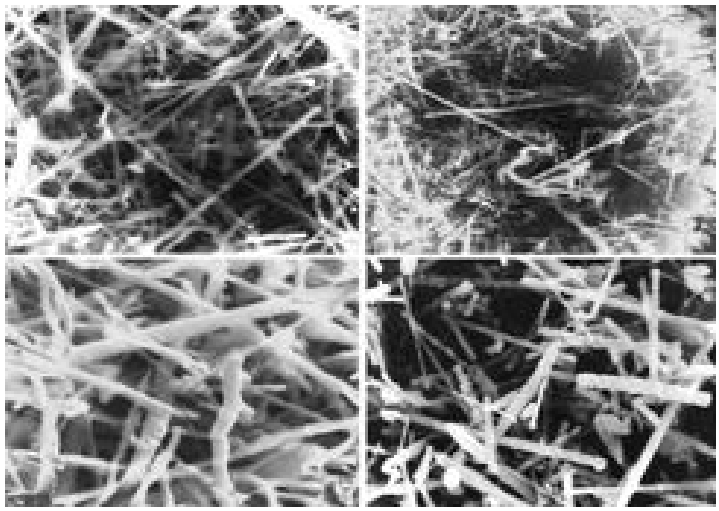


Figure 1. Morphology of whisker crystals of SiC : TWS-200, 2000X (Left up) and 1000X (Right up) ; TWS-400, 2000X (Left down) ; AM7, 200X (Right down)

size and SiO available in great quantity. The need for reaching a threshold size (2–3 μm) of the catalyst droplet before whisker growth is proposed as a possible explanation for the formation of whiskers with uniform size in zones with a high partial pressure of SiO. In the figure 1 is shown morphology of whisker crystals of silicon carbide **[**4].

2 Materials and testing methods

2.1. Raw Materials and additives

The silicon sources in the present work are silicon and ferrosilicon metal. The chemical composition (XRF results) and phase analysis (XRD results) of the raw materials are given in Tables 1 and 2. Specimens were prepared by mixing silicon materials and carbon powder with liquid resin (phenol formaldehyde resin) as a binder.

Material	Al_2O_3	SiO_2	Fe	Si	C	CaO	Particle Size (mm)
Power carbon	10	5	....	....	80	5	0-0.15
Ferrosilicon Metal	....	....	22	75	2	....	0-0.05
Silicon Metal	....	....	1.5	97	1.0	...	0-0.05
Phenol Resole Heated at 800 °C	....	....	....	....	40	....	....

Table 1. Chemical composition of raw materials (XRF results)

Material	Major phase	Medium phase	Minor Phase(s)
Power carbon	Graphite	-------	Al_2O_3, SiO_2
Ferrosilicon Metal	$FeSi_2$	Si	-------
Silicon Metal	Si	-------	-------

Table 2. Phase analysis of raw materials (XRD results)

2.2. Procedures

A twin blade mixer was used for dry mixing and kneading. The raw materials were dry mixed for 5 min and then the resole liquid was added gradually. Mixing continued for another 5 min. The mixture was packed into cylinder metal moulds with a dimension of 50*50 mm and formed under pressure of 4 MPa. Pressed samples were cured at 200 ºC for 2 h and fired at three temperatures (1100 ºC, 1400 ºC or 1500 ºC) for 2 h in a coke environment to avoid oxidizing atmosphere. Study of micrographic (SEM and TEM), phase analysis (XRD) and infrared spectroscopy (FTIR) were carried out on fired samples.

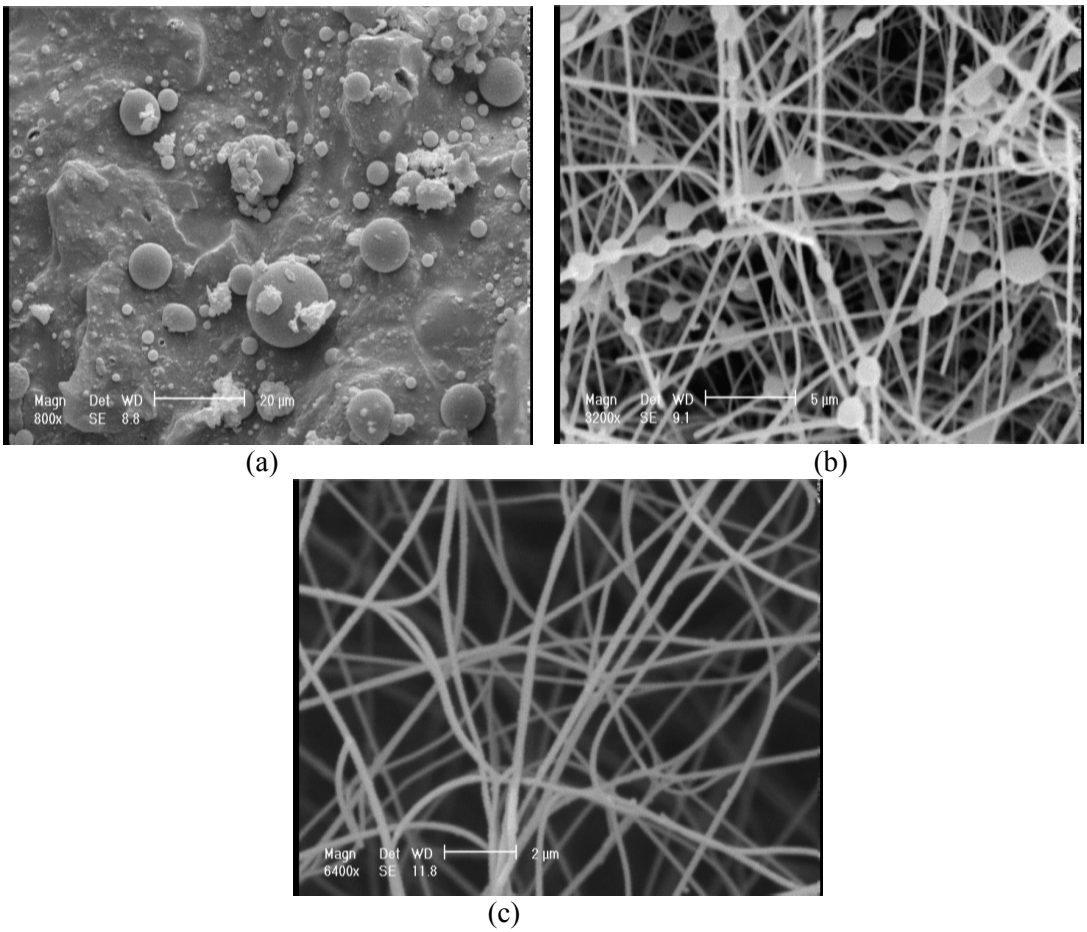
An X-ray diffraction (XRD) instrument was used for phase analysis. In order to study precisely the phases, the XRD experiments were carried out with a rate of 0.04 degrees/sec between 5-80 degrees (2Θ). Scanning electron microscopy (SEM, Philips XL30) was used for microstructure investigations. X-ray florescence (XRF) was used for elemental analysis and oxides content calculations (Table 1). Also, for investigating of chemical bonds Flourier transmittance infrared (FTIR) test was used by instrument of FTIR with broker model and KBr sampling method. Thermal analysis of the sample containing ferrosilicon was investigated by simultaneous thermal analysis (STA , R500) with α-Al_2O_3 as the reference material in argon atmosphere up to1400 ºC at a heating rate of 10 ºC/min.

3 Results

3.1. SEM microstructure

Figure 2 shows microstructure of the specimens fired for 2 h at 1100 ºC, 1400 ºC and 1500 ºC. It illustrates the formation of whiskers in both specimens fired at 1400 ºC and 1500 ºC for

2 h. These whiskers of nano-sized diameter developed from metal particles in the microstructure.



(a) (b)

(c)

Figure 2. Micrograph of Si-C-resole composites containing of ferrosilicon metal heated for 2 h at (a) 1100 ºC , (b) 1400ºC and (c) containing silicon metal heated at 1500 ºC , showing SiC whiskers of about 80-200 nanometers in diameter in the microstructure

SEM photomicrographs revealed that whiskers of nano sized diameter developed in the specimens fired at 1400 ◦C and 1500 ºC (Fig. 2). In fact, at high temperatures of 1400 ◦C and 1500, the driving force is high enough for the formation of SiC whisker to be produced in the specimen containing 6 wt. % ferrosilicon metal and 5wt.% silicon metal, as shown in Fig. 2.

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3.2. XRD results

XRD results just show peaks of SiC in the samples fired at 1400 ºC and 1500 ºC for 2 h (Figs. 3 and 4)

3.3. EDS Analysis on SEM micrograph

Fig. 5-b shows EDS analysis on the nucleation position of whiskers (A point) in a specimen containing silicon and, fired at 1400 ºC for 2 h, confirming the presence of Si and carbon. The spot size of the analyzer is 350 nm, while the whisker diameter is about 100-200 nm. Hence, some carbon is detected from the background which is higher than the amount of Silicon present. The EDS analysis confirms that the formed whiskers are silicon carbide nano whiskers. Also, it confirms the presence of Fe along with Si and C. In the other word, it

confirms that the formation mechanism of SiC is VLS, which in iron (Fe atoms) are as catalyst.

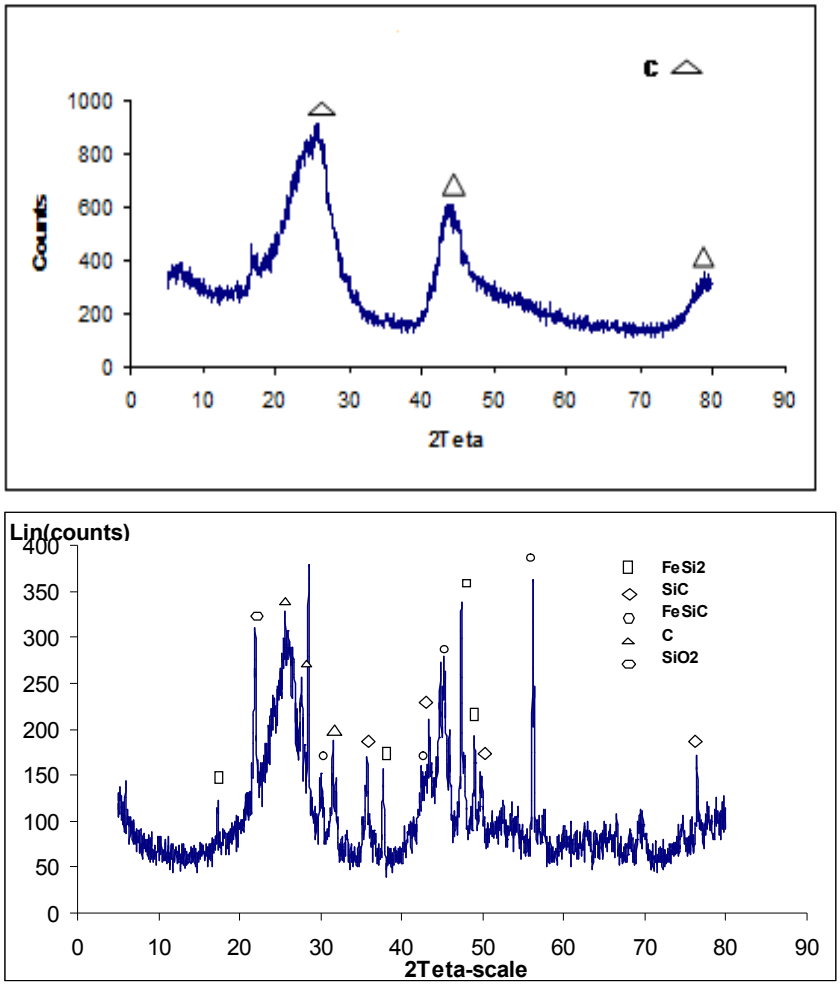


Figure 3. XRD results of the specimen Si-C-resole composites fired for 2 h at 1100 ºC (above) and at 1400 ºC (down)

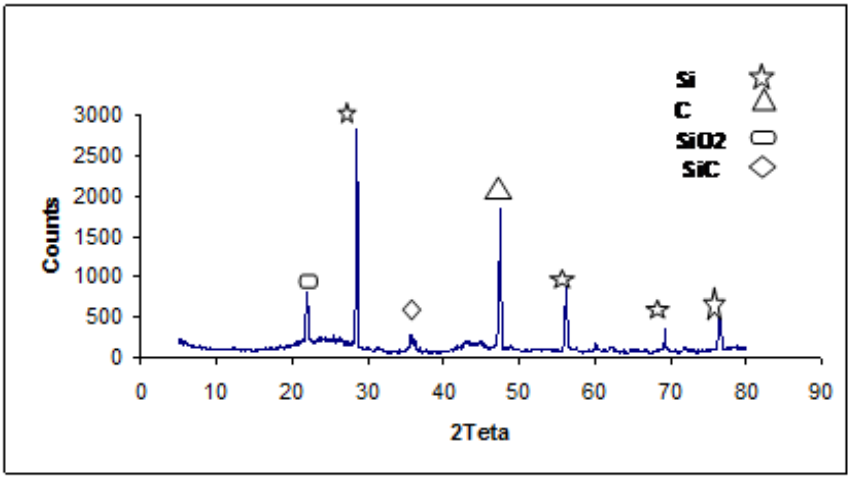
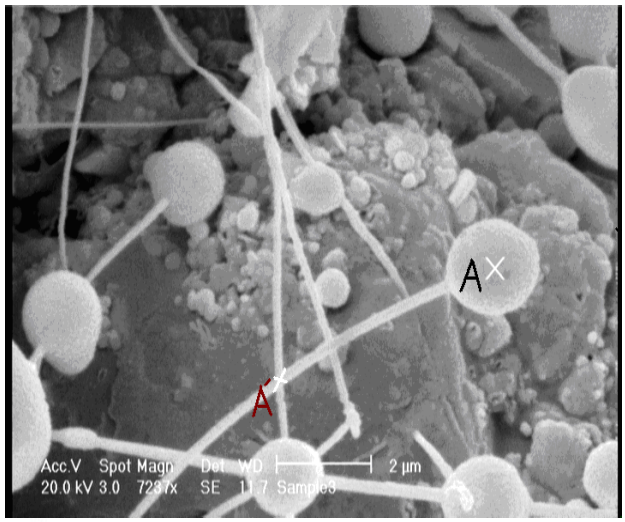
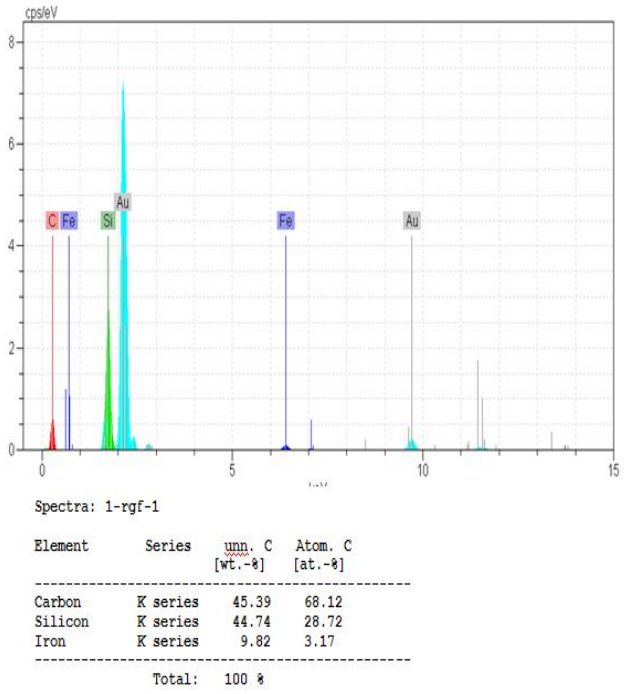


Figure 4. XRD results of the specimen Si-C-resole composites fired for 2 h at 1500 ºC





Spectra: 1-rgf-1

Element	Series	unn. C [wt.-%]	Atom. C [at.-%]
Carbon	K series	45.39	68.12
Silicon	K series	44.74	28.72
Iron	K series	9.82	3.17
	Total:	100 %	

Figure 5.Micrograph of the Si-C-resole composite containing 5 wt. % silicon and fired at 1400 ºC for 2 h and EDS analysis on the tip of whisker (A point)

3.4. Thermal analysis (STA results)

In order to investigate the interaction of silicon and carbon sources, thermal analysis using a simultaneous thermal analysis (STA) was performed for Si-Carbon-Resole composite containing ferrosilicon in argon atmosphere upto1400 ºC at a heating rate of 10 ºC/min. The STA curve has been shown in Figure 6. It confirms that SiC whiskers were formed by the VLS mechanism (vapor–liquid–solid) using iron (ferrosilicon metal) as catalyst at above 1300 ºC.

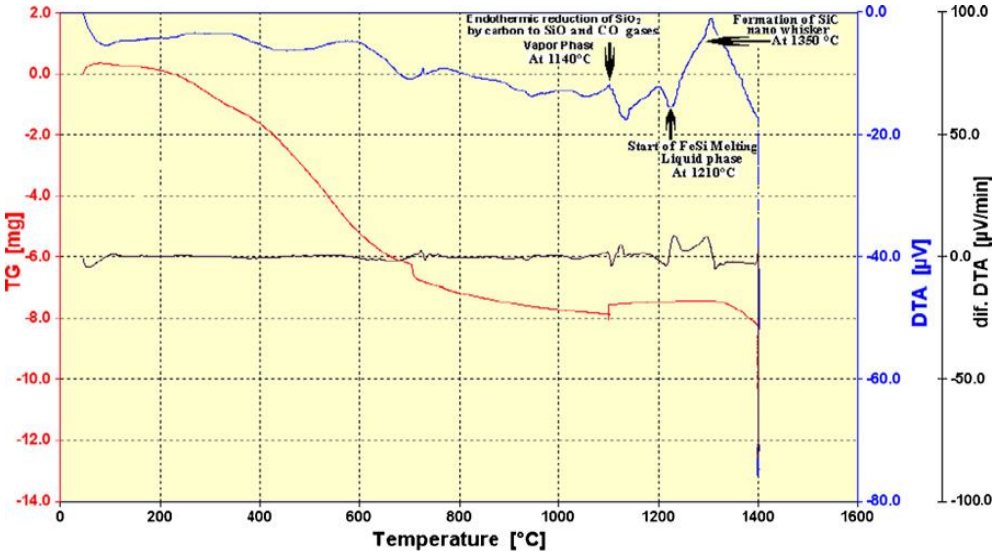


Figure 6. STA curve of Si-C-resole composite containing ferrosilicon, heated up to1400 ºC in argon atmosphere. The formation of SiC by the VLS mechanism using iron (ferrosilicon metal) as catalyst at above1300 ºC

According to the STA curve, it is demonstrated the formation of SiC based on VLS mechanism (Fig. 6). In the VLS mechanism, V stands for vapor feed gases such as SiO and CO gases, L for liquid catalyst (ferrosilicon droplet) and S for solid carbon substrate. The STA curve has two endothermic peaks and one exothermic peak. The first and second endothermic peaks related to generate SiO gas (V) and form catalyst droplet (L), respectively. The exothermic peak last one, related to form SiC. So, it seems at about 1300 ºC solid catalyst particle melts and forms the liquid catalyst ball.

It should be noted that the melting point of ferrosilicon metal (FeSi75) is 1210–1310 ºC. Therefore, the firing temperature is an important factor for the formation of SiC and the temperature of 1100 ºC is not enough for the formation of SiC. So, it needs at least 1300 ºC as a starting point of reaction. Therefore, these whiskers were not observed in the samples heated at 1100 ºC. According to XRD results, the spectra just proved phase SiC in the samples heated at 1400 ºC and 1500 ◦C.

4 Conclusions

1- EDS analysis on whiskers observed by SEM confirms the presence of Si and C; i.e., the presence of SiC.

2- According to XRD results, the spectra just proved phase SiC in the samples heated at 1400 ºC and 1500 ºC.

3- The STA curve confirms that SiC whiskers were formed by the VLS mechanism (vapor–liquid–solid) using iron (ferrosilicon metal) as catalyst at above 1300 ºC.

References

[1] Barino S.M., Krylov A.V. et al, Effect of the size SiC whiskers on the toughness of Alumina based composite materials, Refractories and Industrial ceramic , Vol. 34 , No. 3,4.

[2] In Situ Production of Silicon Carbide Reinforced Ceramic Composite, WO/1991/004234, 1991

[3] Yongging Y.W., Fu. and Du. Hejun, SiC whiskers toughened Al2O3-(Ti,W)C ceramic matrix composites , School of Mechanical and Production Engineering , Nanyang Technological University, 630798, 2001.
[4] Kelley W.H.II , Thermal Shock Resistance of Mullite –Based SiC –whisker composite , Air force Inst. of Tech. Wright-Patterson, 1986.