Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 31 (2011) 2677–2685
www.elsevier.com/locate/jeurceramsoc

Formation of nano SiC whiskers in bauxite–carbon composite materials and their consequences on strength and density

E. Karamian [a,*], A. Monshi [a], A. Bataille [b], A. Zadhoush [c]

[a] Department of Materials Engineering, Isfahan University of Technology (IUT), Isfahan 84156-83111, Iran
[b] UMET, Unité Matériaux et Transformations, UMR CNRS 8207, University of Lille 1 (USTL), F-59655 Villeneuve d'Ascq Cedex, France
[c] Department of Textile Engineering, IUT, Isfahan 84156-83111, Iran

Available online 9 March 2011

Abstract

SiC whisker is excellent in characteristics such as specific strength and chemical stability, and is useful as a composite reinforcing material. In this paper, the effect of the formation of in situ nano SiC whiskers on strength and density of bauxite–carbon composites was studied. Samples were prepared composed of 65 wt.% bauxite, 15 wt.% SiC-containing material, 10 wt.% coke, 10 wt.% resole and different values of silicon additives. The pressed samples were cured at 200 °C (2 h) and fired at 1100 °C and 1400 °C (2 h). XRD, SEM, TEM, EDX, FTIR and STA were used to characterize the samples. These characterizations indicated that SiC nano whiskers, 50–90 nm, are single crystalline β-SiC with mechanism of the formation VLS. So, firing temperature is an important factor. As, SiC nano whisker was formed at 1400 °C and improved CCS values up to four times in sample containing 6 wt.% ferrosilicon.

Keywords: Microstructure; Strength; Carbon; SiC whisker; Bauxite

1. Introduction

$Al_2O_3{\cdot}SiO_2$–SiC–C resin bonded composites form a very important class of new composites for such iron making applications as iron and slag runners in blast furnaces, furnace bottom, and electric-furnace spouts.[1] They can be evolved from high performance chamotte–carbon and bauxite–carbon composites. This class of composites shows not only superior slag corrosion and erosion (wear) resistance, but also excellent thermal shock resistance and mechanical properties. These composites consist mainly of alumina silicate and carbon bonds formed by carbonization of phenol resins (resole) during firing of the composites (Fig. 1).[1,2]

Carbon does not wet molten metal and will not melt, which makes it appropriate for refractory use. The major drawback is its oxidation at low temperatures (above 650 °C), which results in lower density, high porosity and reduced strength Mostly silicon and aluminum, called antioxidants, are used as sintering agents to improve the mechanical strength and abrasion resistance of the carbon-containing refractory under oxidation conditions.[1,3] The effect of silicon particle size on the properties of alumina–carbon refractory brick has been studied. The added silicon reacts under the reducing atmosphere with carbon in the refractory brick to produce a β-SiC bond which improves the mechanical strength and abrasion resistance of Al_2O_3–C bricks under oxidation conditions. However, the mechanism for the influence of β-SiC bond on mechanical strength has not yet been clarified.[4]

Fangbao et al.[5] showed that SiC additions in the range of 4–16% improved the mechanical properties as well as thermal shock resistance of bauxite-based SiC-containing castable. Thermodynamic investigations showed that SiC had a large influence on preventing carbon oxidation of Al_2O_3–SiC–C bricks. SiC behavior in Al_2O_3–SiC–C bricks is illustrated by the reactions shown in Eqs. (1) and (2) below.

$$SiC(s) + CO(g) = SiO(g) + 2C(s) \quad (1)$$

$$SiO(g) + CO(g) = SiO_2(s) + C(s) \quad (2)$$

The overall reaction involves $SiC + 2CO(g)$ to produce $SiO_2 + 3C$. This demonstrates that SiC can prevent oxidation of carbon ($C + 1/2O_2(g) = CO(g)$).[6]

* Corresponding author.
E-mail addresses: ekaramian@iaun.ac.ir, ebkaramian@yahoo.com (E. Karamian).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.02.019

The improved strength and reinforcement in ceramics and composites containing silicon and carbon fired at high temperatures are related to the development of nano-sized SiC whiskers.[7] SiC whisker is excellent in characteristics such as specific strength, specific modulus, heat resistance, chemical stability, etc. and is useful as a composite reinforcing material. 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 $m^{1/2}$ to 8.5 MPa $m^{1/2}$ with the addition of 20 v/o whiskers. This was accompanied by fracture strengths of 700–800 MPa versus 400 MPa in unreinforced alumina. 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.[8]

2. Materials and methods

2.1. Raw materials and additives

Samples were prepared using the formulation shown in Table 1. Ferrosilicon and silicon powders in the ranges 2–6 wt.% and 1–5 wt.%, respectively, were used as additives. The chemical composition and phase analysis of the raw materials and additives are given in Tables 2 and 3, respectively.

Table 1
Formulation of raw materials.

Chinese coarse bauxite (1–3 mm)	Chinese fine bauxite (0–1 mm)	Crushed SiC-containing material	Fine coke	Liquid resole
20 wt.%	45 wt.%	15 wt.%	10 wt.%	10 wt.%

Table 3
Phase analysis of raw materials and additives (XRD results).

Material	Major phase	Medium phase	Minor phase(s)
Chinese bauxite	α-Al_2O_3	Mullite ($3Al_2O_3{\cdot}2SiO_2$)	TiO_2, SiO_2
Crushed sagger	α-SiC	Mullite	α-Al_2O_3
Fine coke	Carbon	–	Al_2O_3, SiO_2
Ferrosilicon metal	$FeSi_2$	Si	–
Silicon metal	Si	–	–

2.2. Procedures

A twin blade mixer was used for dry mixing and kneading. The raw materials were dry mixed for 5 min, to which the liquid resole was then added gradually followed by mixing for another 5 min. The mixture was then packed into metal mould with the dimensions 50 mm × 50 mm × 50 mm and later formed by a hydraulic pressing under a pressure of 4 MPa. The pressed samples were cured at 200 °C for 2 h. Finally, the samples were fired at 1100 °C and 1400 °C for 2 h in a coke environment. The cured and fired specimens were characterized according to ASTM (C0133-97R03 for CCS test and C0020-00R05 for AP and BD tests). A few of the specimens were also subjected to X-ray diffraction (XRD), scanning electron microscopy (SEM) and EDX analysis. CCS was measured by Hydraulic Testing Machine type Amsler model D3010/2E. BD was determined according to Archimedes method.

Table 2
Chemical composition of raw materials and additives (XRF results).

Material	Al_2O_3	SiO_2	CaO	TiO_2	SiC	C	Si	Fe	S	Particle size (mm)
Chinese bauxite	80	8.9	0.55	4.95	–	–	–	–	–	0–11–3
Crushed sagger	42	18	–	–	38	–	–	–	–	0–3
Fine coke	10	5	–	–	–	80	–	–	1.0	0–0.15
Ferrosilicon metal	–	–	–	–	–	2	72	23	0.1	0–0.15
Silicon metal	–	–	–	–	–	0.8	98	1.0	–	0–0.15

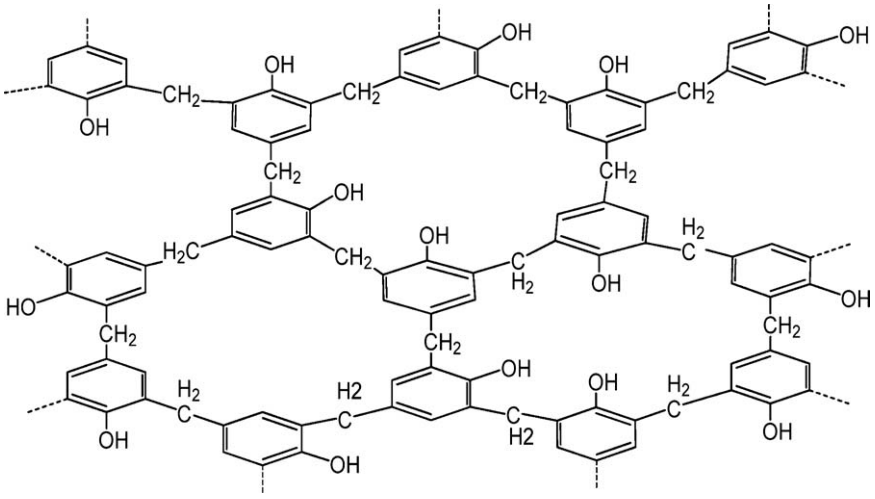


Fig. 1. Resit structure.

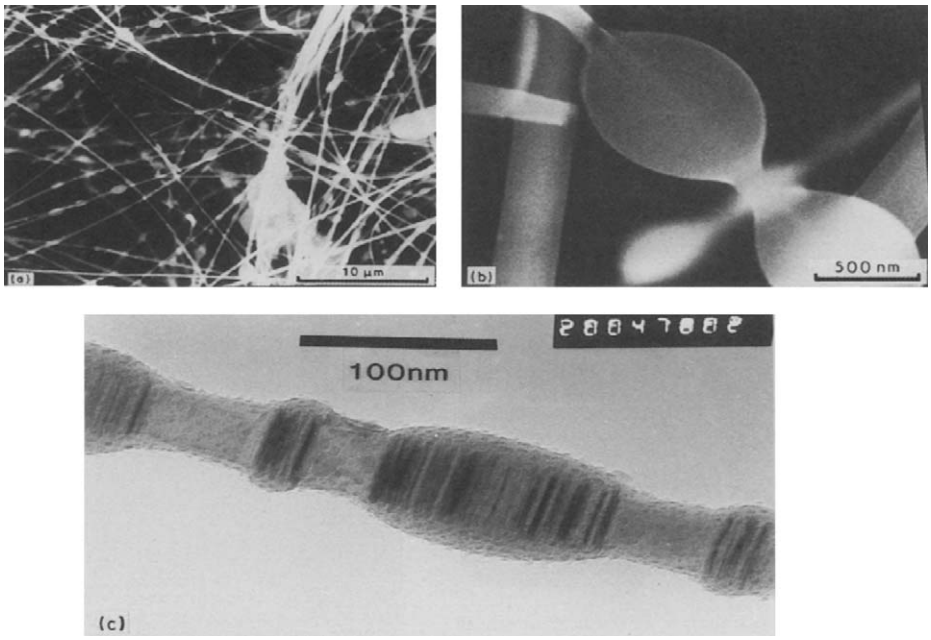


Fig. 2. The amorphous coating occasionally formed large bulbous regions on the Isolite whiskers. (a) General SEM view of whiskers, some containing bulges. (b) Higher magnification SEM image of a bulged whisker. A whisker can be seen to continue through the bulges. (c) TEM imaging shows that a thickening of the coating is associated with transverse defects in some whiskers.

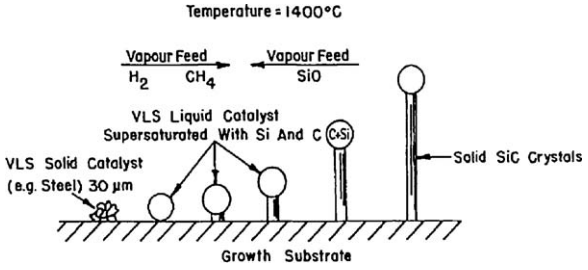


Fig. 3. The formation of SiC whisker by the vapor–liquid–solid (VLS) mechanism using Fe catalyst.

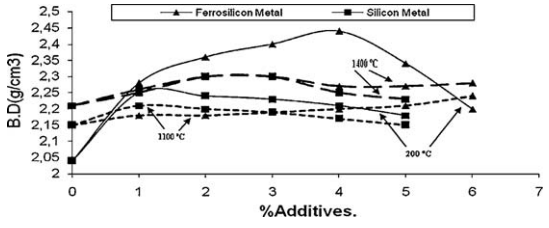


Fig. 5. Effect of additives on BD of fired bauxite–C composites fired for 2 h at different temperatures.

An X-ray diffraction (XRD) instrument was used for phase analysis. A scan rate of 0.04°/s and a 2 theta range between 5° and 80° was used for the XRD experiments. Scanning electron microscopy (SEM, Philips XL30) was used for microstructural investigations. X-ray florescence (XRF) was also used for elemental analysis and oxide content calculations (Table 2). FTIR instrument (model Bomem MB 100 series) was used between 400 and 4000 cm^{-1} (medium IR) for chemical bonding studies and some phase formation with equivalent bonds. The specimens were prepared using the KBr method. Energy dispersive X-ray

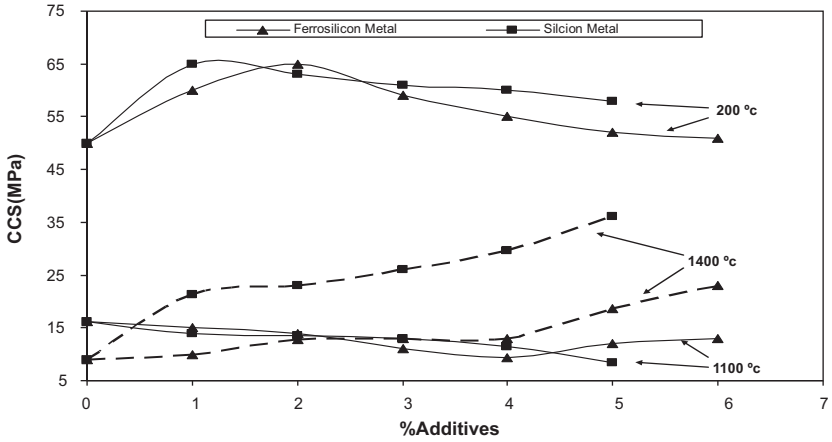


Fig. 4. Effect of additives on CCS of the specimens fired at different temperatures for 2 h.

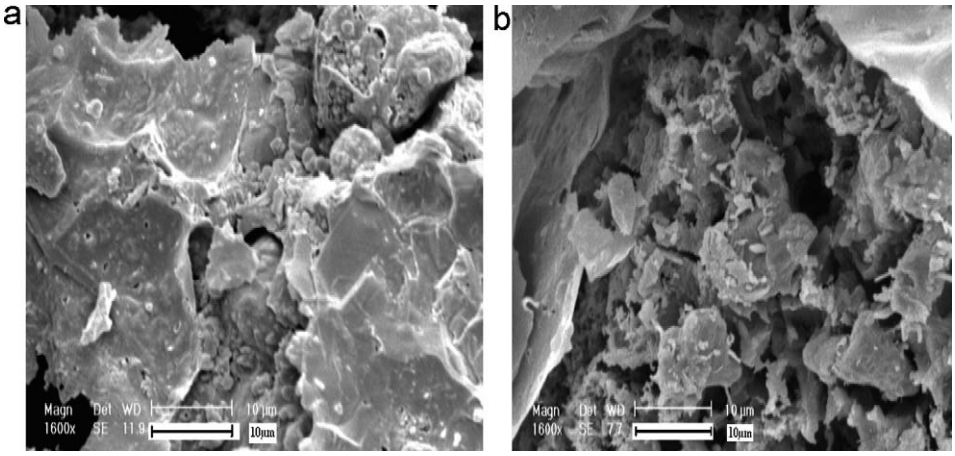


Fig. 6. Micrograph of bauxite–C composites fired at 1100 °C for 2 h containing 5 wt.% silicon (a) and containing 6 wt.% ferrosilicon (b). There are not SiC whiskers in the microstructure.

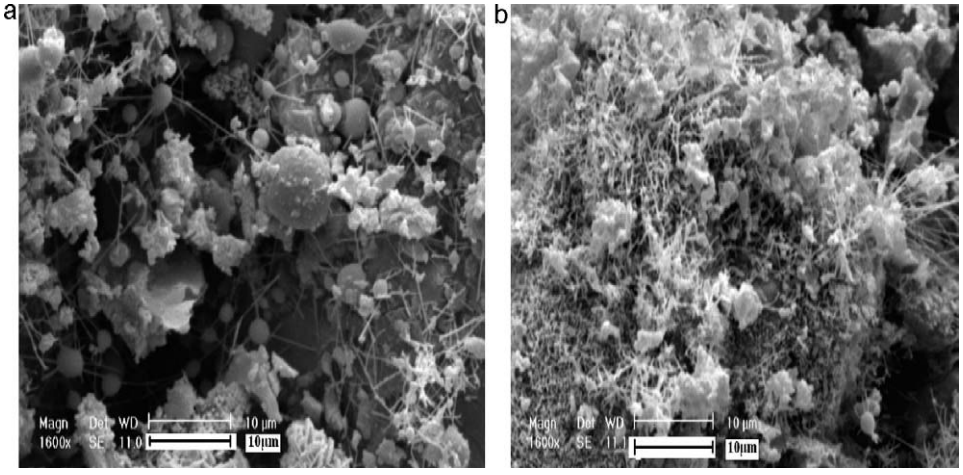


Fig. 7. Micrograph of bauxite–C composites fired at 1400 °C for 2 h containing 5 wt.% silicon (a) and containing 6 wt.% ferrosilicon (b). Nano-sized SiC whiskers developed in the microstructure.

microanalysis (EDX) was performed by a SEM (Philips XL30) instrument. Transition electron microscopy (TEM, FEI Tecnai G2 20) was used for microstructural investigations of nano SiC whiskers. Thermal analysis of bauxite–SiC–C composite containing ferrosilicon was investigated by simultaneous thermal analysis (STA, R500) with α-Al_2O_3 as the reference material in argon atmosphere up to 1400 °C at a heating rate of 10 °C/min.

3. Theory

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.[9] Increasing SiC whisker content decreased 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.[10]

Synthesis of submicron silicon carbide powders with silicon powder and phenolic resin was carried out by Shi et al. The mechanism of the silicon carbide formation is based on

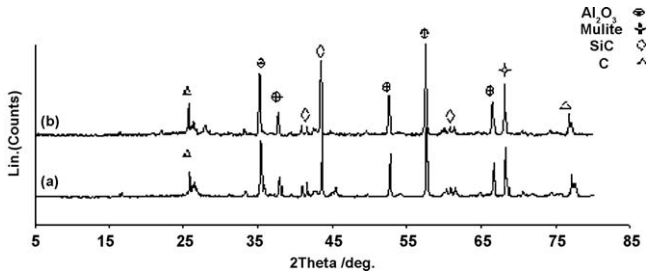


Fig. 8. XRD results of fired bauxite–C composites fired at 1100 °C for 2 h with (a) 5 wt.% silicon as additive and (b) without additive. The new SiC peaks are not absorbed in the sample containing silicon additive.

liquid–solid reaction between liquid silicon and carbon derived from phenolic resin.[11] β-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

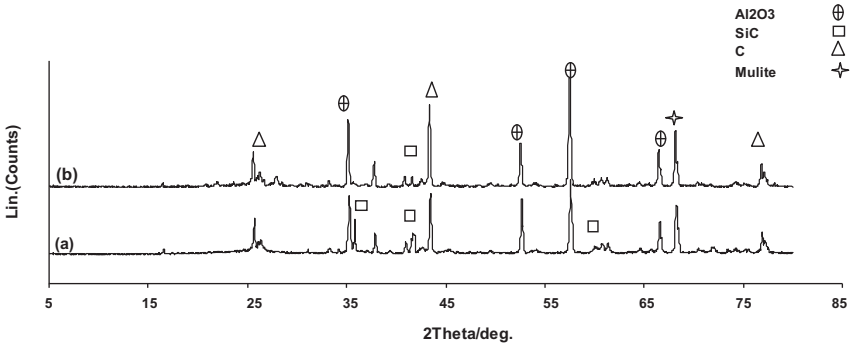


Fig. 9. XRD results of fired bauxite–C composites fired at 1400 °C for 2 h (b) with 5 wt.% silicon as additive and (b) without additive. The new SiC peaks are observed in the sample containing silicon additive.

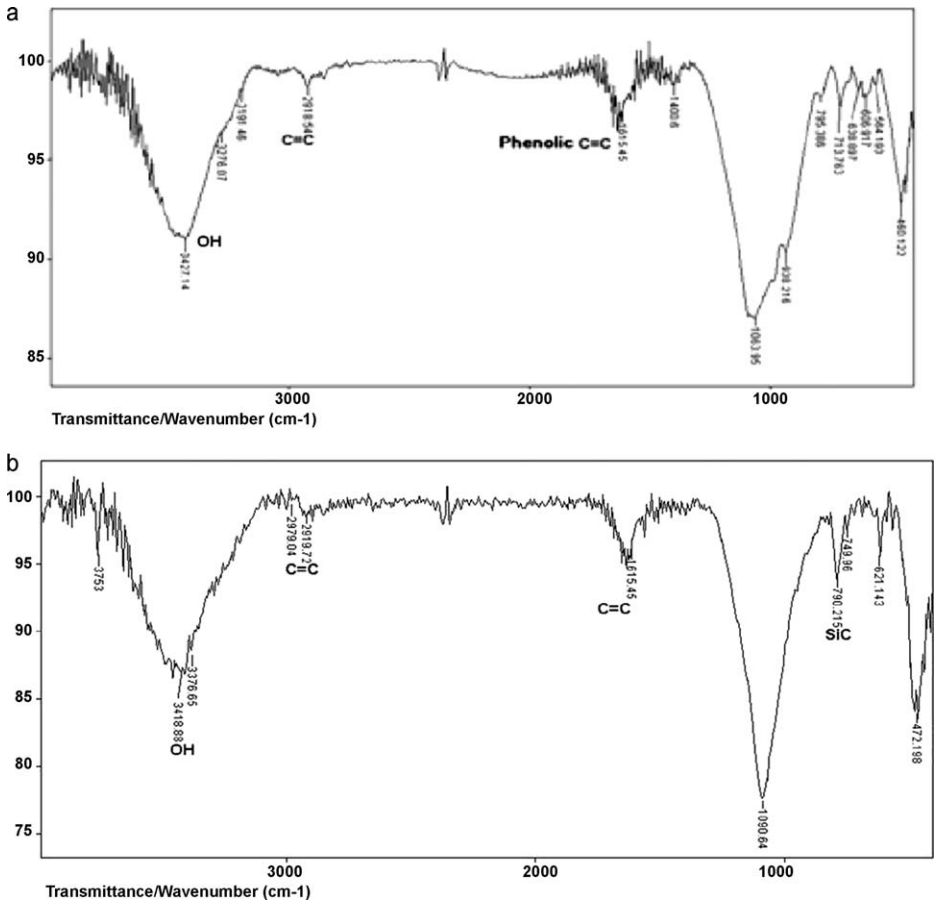


Fig. 10. FTIR spectra of the specimen containing silicon metal and fired for 2 h (a) at 1100 °C (without the SiC phase band) and (b) at 1400 °C (observation of the SiC phase band).

growth was produced where there were Fe droplets of appropriate 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.[12] Morphology of whisker crystals of silicon carbide is shown in Fig. 2.

In the VLS mechanism, V stands for vapor feed gases, L for liquid catalyst and S for growth carbon substrate. At about 1400 °C solid catalyst particle melts and forms the liquid catalyst ball. Silicon and carbon atoms in the vapor feed are accreted to the surface by the liquid catalyst, which soon becomes supersaturated, and SiC precipitates from liquid catalyst (Fig. 3).[13]

Table 4
Wave number of chemical bonds.

Chemical bond	OH	C=C	Phenolic C=C	Si–C
Wave number (cm^{-1})	3425	2918	1615	780–820

4. Results

4.1. CCS and BD results

Fig. 4 shows the effect of the additives on the cold crushing strength (CCS) of the specimens fired at different temperatures (200 °C, 1100 °C and 1400 °C) for 2 h. Fig. 5 illustrates the influence of the additives on BD. Silicon and ferrosilicon generally increased BD values in all heat treatments and at the temperatures 200 °C, 1100 °C and 1400 °C.

4.2. SEM microstructure

Fig. 6 shows microstructure of the specimens fired at 1100 °C for 2 h containing 5 wt.% silicon and 6 wt.% ferrosilicon. Fig. 7 illustrates the formation of whiskers in both specimens fired at 1400 °C for 2 h.

4.3. XRD results

XRD results show high peaks of carbon (graphite) in both samples fired at 1400 °C and 1100 °C for 2 h (Figs. 8 and 9). But, there are the new peaks of SiC just in the case of the specimen containing 5 wt.% silicon fired at 1400 °C (Fig. 9).

4.4. FTIR spectroscopy

Fig. 10 shows the FTIR spectra of the specimens containing silicon and fired at 1100 °C and 1400 °C for 2 h. Both patterns

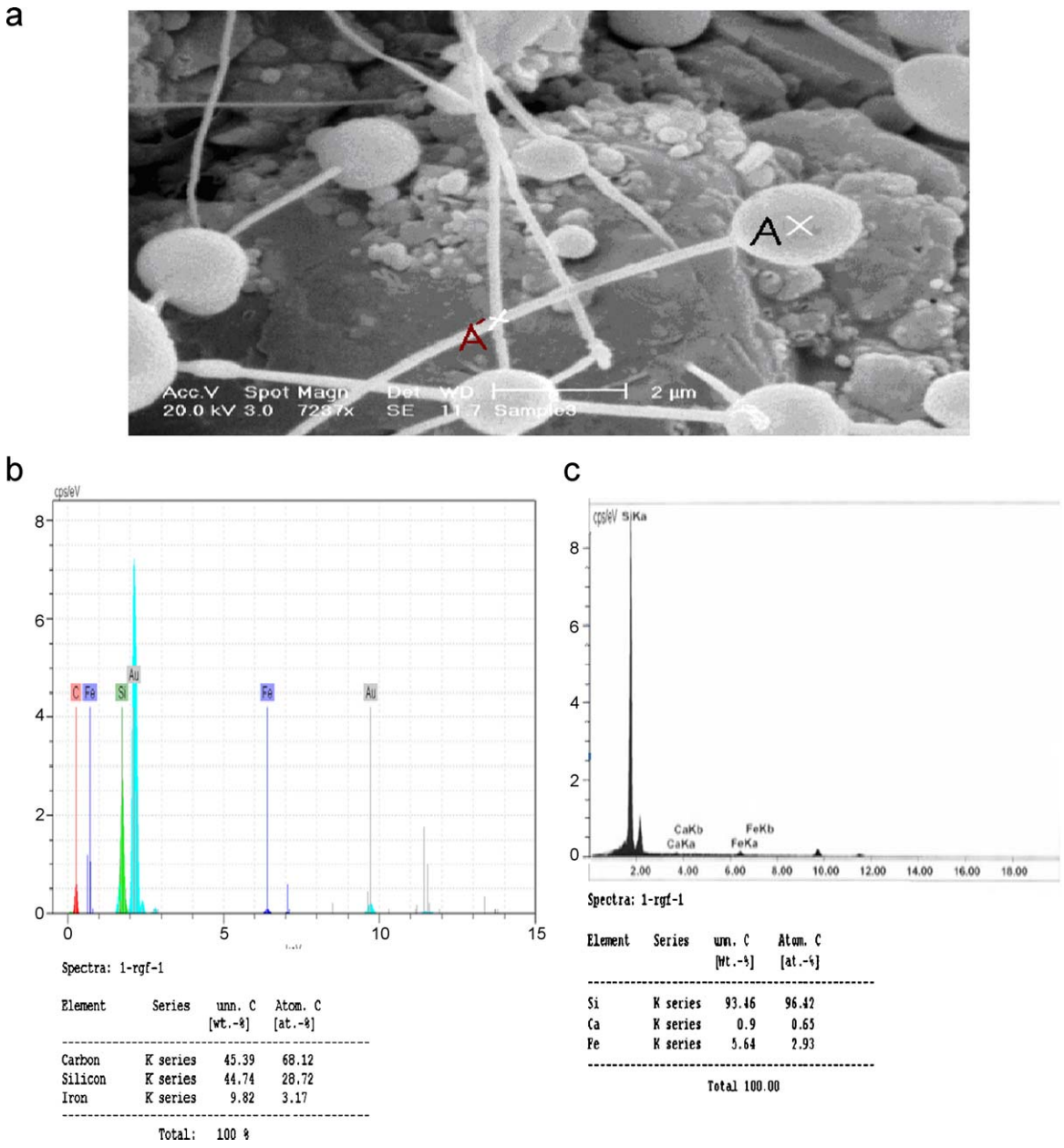
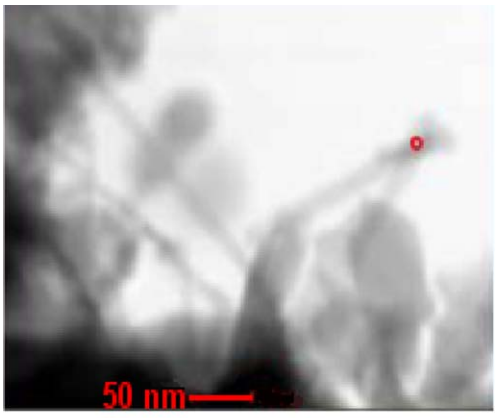
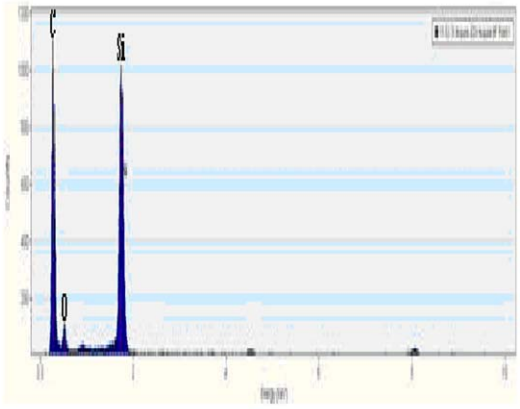


Fig. 11. (a) Micrograph of the bauxite–C composite containing 5 wt.% silicon and fired at 1400 °C for 2 h (b) EDX analysis on the tip of whisker (A point). It confirms the presence of Fe along with Si and C. In fact, it proves that the mechanism of the formation of SiC nano whisker is a VLS type one, for which present iron atoms (Fe) act as catalyst. (c) EDX analysis on whiskers (A′ point). It confirms the presence of Si and carbon, i.e., SiC, is observed.





Quantification Results

Correction method: Thickness

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor	Absorption Correction
O(K)	12.09	19.57	0.40	0.49	1.600	1.000
Al(K)	3.19	3.06	0.16	0.92	1.100	1.000
Si(K)	82.57	76.11	0.76	0.92	1.000	1.000
Ca(K)	0.88	0.56	0.09	0.98	1.400	1.000
Ti(K)	1.24	0.67	0.12	0.98	1.229	1.000

Fig. 12. TEM micrograph and EDX analysis of nano whiskers in bauxite–C composite containing 5 wt.% silicon fired at 1400 °C for 2 h. In the EDX analysis spectrum on whisker, the presence of Si and carbon, i.e., SiC, is observed.

contain several transmittance bands, which have been assigned to individual structural units as listed in Table 4. The specimen fired at 1100 °C does not show any band of SiC phase while that fired at 1400 °C shows the SiC phase band.

4.5. EDX analysis on SEM microstructure

Fig. 11b shows EDX analysis on the tip of whisker (A point) in a specimen containing silicon and fired at 1400 °C for 2 h. It confirms the presence of Fe along with Si and C. In fact, it proves that the mechanism of the formation of SiC nano whisker is a VLS type one, for which present iron atoms (Fe) act as catalyst droplet. Fig. 11c shows EDX analysis on whisker observed in the SEM microstructure (Fig. 11a). It confirms the presence of Si and carbon, i.e., SiC, is observed. 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 Si present. The EDX analysis confirms that the formed whiskers are silicon carbide nano whiskers.

4.6. TEM microstructure and EDX analysis

Fig. 12 shows TEM micrograph and EDX analysis of nano whiskers in bauxite–C composite containing 5 wt.% silicon, fired at 1400 °C for 2 h. The EDX analysis on whisker observed in the TEM microstructure confirms the presence of Si and carbon. In the order word, the EDX analysis confirms that the formed whiskers are silicon carbide. Fig. 13 shows TEM micrograph and EDX analysis of sole nano whisker in bauxite–C composite containing ferrosilicon fired at 1400 °C for 2 h. EDX analysis on the tip of whisker observed in the TEM confirms vigorously the presence of Fe atoms on the tip of whisker. In fact, it confirms that the tip of the whisker has been as catalyst droplet in the formation SiC nano whisker by VLS mechanism. In the other word, it proves that the mechanism of the formation of SiC nano whisker is a VLS type one, for which present iron atoms (Fe) act as catalyst droplet.

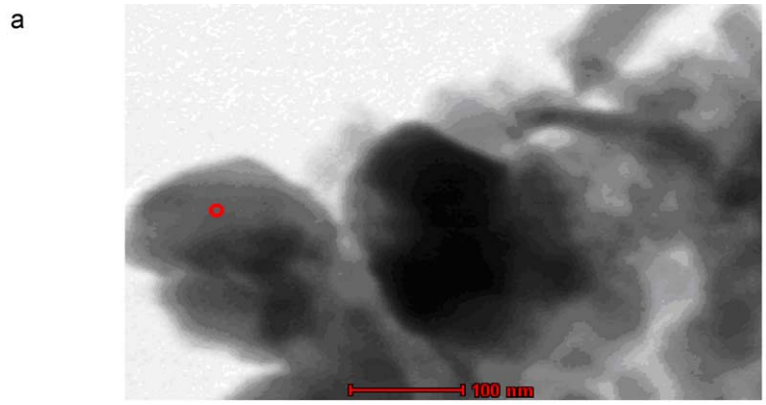
4.7. Thermal analysis (STA results)

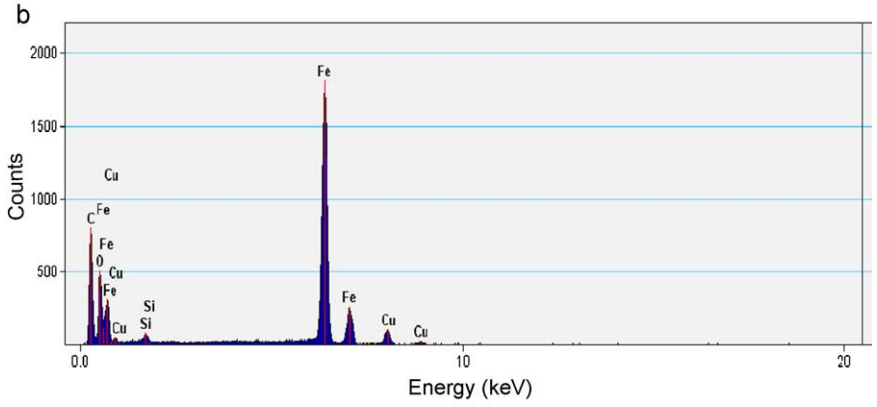
In order to investigate the interaction of silicon and carbon sources, thermal analysis using a simultaneous thermal analysis (STA) was performed for bauxite–SiC–C composite containing ferrosilicon in argon atmosphere up to 1400 °C at a heating rate of 10 °C/min. The STA curve has been shown in Fig. 14. It confirms that SiC whiskers were formed by the VLS mechanism (vapor–liquid–solid) using iron (ferrosilicon metal) as catalyst at above 1300 °C.

5. Discussion

Silicon and ferrosilicon generally increase bulk density in all heat treatments of 200 °C, 1100 °C and 1400 °C.

SEM photomicrographs revealed that whiskers of nano sized diameter developed in the specimens fired at 1400 °C as a result of using 6 wt.% ferrosilicon and 5 wt.% silicon (Fig. 7). In fact, at a temperature of 1400 °C, the driving force is high enough for SiC whisker to be produced in the specimen containing 6 wt.% ferrosilicon metal and 5 wt.% silicon metal, as shown in





Quantification Results

Correction method: Thickness

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor	Absorption Correction
O(K)	12.68	33.38	0.19	0.99	1.600	1.000
Si(K)	1.08	1.63	0.05	0.92	1.000	1.000
Fe(K)	86.22	64.98	0.47	0.99	1.740	1.000

Fig. 13. (a) TEM micrograph of sole nano whisker in bauxite–C composite containing 6 wt.% ferrosilicon fired at 1400 °C for 2 h and (b) EDX analysis on the tip of whisker. It confirms vigorously the presence of Fe atoms on the tip of whisker. In fact, it proves that the mechanism of the formation of SiC nano whisker is a VLS type one, for which present iron atoms (Fe) act as catalyst droplet.

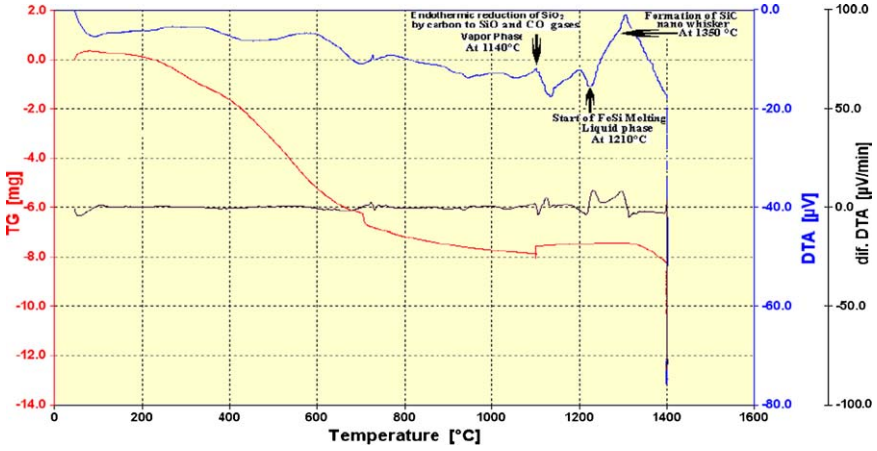


Fig. 14. STA curve of bauxite–C composite containing ferrosilicon, heated up to 1400 °C in argon atmosphere. The formation of SiC by the VLS mechanism using iron (ferrosilicon metal) as catalyst at above 1300 °C.

Fig. 7. The increase in strength in the specimens fired at 1400 °C, shown in Fig. 4, is related to the development of nano-sized whiskers.

According to the STA curve, it is demonstrated the formation of SiC based on VLS mechanism (Fig. 14). 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 °C solid catalyst particle melts and forms the liquid catalyst ball. It should be noted that the melting point of ferrosilicon metal (FeSi 75) is 1210–1310 °C. Therefore, the firing temperature is an important factor for the formation of SiC and the temperature of 1100 °C is not enough for the formation of SiC. So, it needs at least 1300 °C as a starting point of reaction. Therefore, these whiskers were not observed in the specimens fired at 1100 °C (Fig. 6).

EDX analysis spectra on whiskers observed by SEM (Fig. 11c) and TEM (Fig. 12) confirm the presence of Si and carbon; i.e., the presence of SiC. Also, the EDX analysis spectra on the tip of whisker observed by SEM (Fig. 11b) and TEM (Fig. 13) confirm the presence of Fe atoms. In fact, it proves that the mechanism of the formation of SiC nano whisker is a VLS type one, for which present iron atoms (Fe) act as catalyst droplet. In the other word, it confirms that whisker growth was produced where there were Fe droplets.

The FTIR spectrum of the specimen containing silicon fired at 1400 °C for 2 h shows the band of SiC, the transmittance band at 790–800 cm^{-1},but it does not show any the transmittance band at 790–800 cm^{-1}, band of SiC, in the specimen containing silicon fired at 1100 °C (Fig. 10). It indicates the development of SiC at 1400 °C in a body composed of silicon metal, while it has not developed at the temperature of 1100 °C (Fig. 10a). In addition to studies of FTIR, XRD results proved both nucleation and growth of SiC whisker just in the sample fired at 1400 °C (Figs. 8 and 9).

Maximum values of CCS were observed at 1% silicon and 2% ferrosilicon at a temperature of 200 °C (65 MPa), which is presumably due to the increase in cross-linking. This is a remarkable result for a carbon containing monolithic material (Fig. 4).

According to the hypothesis made in Ref. [5], the formation of β-SiC bond is due to the reaction of Si and C in the microstructural phase. The sources of these carbon atoms are resole and graphite. This bonding provides a network structure which holds the refractory aggregates firmly together, thereby increasing the strength of the monolithic material.

6. Conclusions

1. Maximum strength values (CCS) of bauxite–C composites are observed at a temperature of 200 °C, gradually decreasing at 1100 °C and increasing at 1400 °C as a result of adding silicon and ferrosilicon.
2. At a high temperature of 1400 °C, the addition of silicon or ferrosilicon metal improves strength due to the formation of nano-sized SiC whiskers.
3. The addition of silicon and ferrosilicon metal generally increases bulk density to a certain extent for a given temperature.
4. In addition to XRD results, studies of FTIR spectrum just proved both nucleation and growth of SiC whisker at 1400 °C.
5. EDX analysis spectra on whiskers observed by SEM and TEM confirm the presence of Si and C; i.e., the presence of SiC.
6. Also, the EDX analysis spectra on the tip of whisker observed by SEM and TEM confirm the presence of Fe atoms. In fact, it proves that the mechanism of formation of the SiC whisker is a VLS type one, for which present iron atoms (Fe) act as catalyst droplet. In the other word, they confirm that whisker growth was produced where there were Fe droplets.

References

1. Bosall SB, Henry DK. *Am Ceram Soc* 1985;**13**:331–40.
2. Chan C, Argent BB, Lee WE. *J Am Ceram Soc* 1998;**81**(12):3177–88.
3. Yamaguchi A. *Adv Sci Technol* 2003;**35**:43–51.
4. Akamine K, Suruga T, Yoshitomi J, Asano K.*49th International Colloquium on Composites*. 2006. p. 145–9.
5. Fangbao Y, Rigaud M, Liu X, Zhong X. *Ceram Int* 2004;**30**:801–5.
6. Nishio H, Matsuo A. *Taikabutsu Overseas* 1995;**15**(4):39–46.
7. Zhang X, Xu L, Du S, Han J, Han W, Liu C. *J Alloys Compd* 2008;**466**(1–2):241–5.
8. Hvizdoš P, Rudnayová E, Dusza J, Barinov SM, Krylov AV. *Refract Ind Ceram* 1997;**34**(3):51–6.
9. In situ production of silicon carbide reinforced ceramic composites. WO/1991/004234; 1991.
10. Yongqine Fu, Gu YW, Hejun Du. *Scripta Materials* 2001;**44**(1):111–6.
11. Shi L, Zhao H, Yan Y, Li Z, Tang C. *Powder Technol* 2006;**169**:71–6.
12. Kelley II William H, ADA 179214, Master's thesis, Air Force Inst. of Tech. Wright-Patterson AFB OH (USA), School of Engineering, oai.dtic.mil, 1986.
13. Millewski JV, Gac FD, Petrovic JJ, Skaggs SR. Growth of beta-silicon carbide whiskers by the VLS process. *J Mater Sci* 1985;**20**:1160–6.