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In situ synthesis of nano size silicon carbide and fabrication of C–SiC composites during the siliconization process of mesocarbon microbeads preforms

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Abstract

C–SiC composites with carbon-based mesocarbon microbeads (MCMBs) preforms are a new type of high-performance and high-temperature structural materials for aerospace applications. In the present study, MCMB-SiC composites were fabricated by liquid silicon infiltration (LSI). Physical and mechanical properties such as density, porosity and bending strength were measured before and after siliconization. The results show the C–SiC composites have excellent bending strength, density and porosity of 210 MPa, 2.41 g/cm^3 and 0.62%, respectively. The chemical analysis shows that the composite is composed of 89% SiC, 2% Si and 9% C. The microstructural results also show the existence of two different areas of SiC, one zone of coarse micron size SiC at SiC–Si interface and the other zone consists of fine nano-SiC particles at SiC–C interfaces. The formation mechanism governing the siliconization of porous MCMB preform was also investigated.

Keywords: B. Composite; D. Carbon; Liquid silicon infiltration (LSI); Mesocarbon microbeads (MCMBs)

1. Introduction

Mesocarbon microbeads (MCMBs) as a promising carbon material gained much attention from many researchers [1–3]. The microtexture of MCMBs is usually regarded as global type or Brooks–Taylor type [4,5] with the polyaromatic molecules approximately parallel to one another and perpendicular to the surface of the sphere, which is suitable for the lithium ion insertion and desertion [6]. Therefore, MCMB is a good material for the anode of rechargeable lithium ion batteries and the lithium storage capacity [7].

C–SiC composites are one of the most important ceramic matrix composites. Modern technology makes wide use of C–SiC composites in different fields, including nuclear reactor walls, rocket nozzles, pistons for internal combustion engines, battery electrodes, and friction materials [8–12]. These applications exploit the exceptional properties of carbon such as its excellent mechanical behavior at high temperatures, low reactivity, high-heat capacity, and anisotropic thermal conductivity. C–SiC composites are processed according to: (1) a gas phase route, also referred to as chemical vapor infiltration (CVI), (2) a liquid phase route including the polymer impregnation/pyrolysis (PIP) and liquid silicon infiltration (LSI) also called (reactive) melt infiltration (RMI or MI) processes as well as (3) a ceramic route, i.e. a technique combining impregnation of the reinforcement with a slurry and a sintering step at a high temperature and high pressure [12].

The reactive melt infiltration (RMI), alternatively called liquid silicon infiltration (LSI) process, is an attractive method for fabricating silicon carbide ceramics due to its lower processing temperature, shorter time and near-net shape fabrication capability [13–17]. The process involves the following steps: fabrication of porous carbon preforms as well as infiltration with liquid silicon and chemical reaction to form silicon carbide ceramics. The resulting SiC ceramics are known as reaction-formed SiC (RFSC). The morphology and porosity of the preform and the reactivity of the carbon source are the main factors which affect the fabricating process, the microstructures and the mechanical properties of the reaction-formed SiC [15–23].

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A novel fabrication approach for C–SiC composites utilizes mesocarbon microbeads (MCMB) as a carbon precursor for preparing porous carbon preforms. Extracted from mesophase pitch MCMB has been recognized as excellent precursors to parts with high density and strength, and has recently been used as a matrix for carbon–carbon composites [8]. The ability of MCMB to self-sinter at relatively low temperatures, homogeneous shrinkage, high yield of carbon, and easy graphitization has attracted considerable attention in the literature [8,24–27].

However, no previous studies have been found in the literature using MCMBs as carbon substrate for preparing reaction-formed SiC. In this work, MCMBs without any additives and binders were first used to make a porous carbon preform and then the MCMB-SiC composite was prepared by liquid silicon infiltration. The mechanical and physical properties as well as the microstructure of fabricated MCMB-SiC composite were investigated.

2. Experimental procedure

2.1. Raw materials and preparation of MCMBs

A coal tar pitch with QI was used to prepare MCMBs. Some properties of the coal tar pitch are summarized in Table 1. The coal tar pitch was sealed off in a 2-L stainless-steel reactor. Liquid carbonization was carried out by heating the system up to 410 °C at a rate of 1.5 °C/min with continuous stirring of about 370 rpm and maintaining at the final temperature for 7 h for each sample before the system was annealed naturally to room temperature. MCMBs generated in the heat-treated pitch were separated out with toluene using a standard Soxhlet apparatus and the isolated spheres were dried under 60 °C for 15 h before further use. The yields, size and ash content of the as-received MCMBs were also summarized in Table 2. The fabrication of MCMB was shown at Fig. 1.

2.2. Observation of MCMBs

The MCMBs in the matrix of heat-treated pitch were observed directly using optical microscope (OM, OLYMPUSBX51L) under plane-polarized light. The isolated MCMBs powders were dispersed in ethanol using ultrasonicator and spread on a glass carrier. Then their sizes and surfaces were analyzed with a transmission electron microscope (TEM, PHILIPS) after being gilded in vacuum.

Table 1
Properties of coal tar pitch.

Softening point (°C)	Solubility (wt.%)			
	HS	HI–TS	TI–QS	QI
78	19.6	58.8	16.9	4.7

HS, hexane soluble.
HI–TS, hexane insoluble–toluene soluble.
TI–QS, toluene insoluble–quinoline soluble.
QI, quinoline insoluble.

Table 2
The characteristics of the as-received MCMBs.

Particle size (μm)	10% < 1 50% < 5.34 90% < 14.22
Yield (wt.%)	17.6
Ash content (wt.%)	0.76

2.3. Carbon porous preform preparation

First MCMBs were stabilized at 100 °C for 12 h in air. Then the samples were compacted by cold isostatic press (CIP) under a pressure of 150 MPa. In the next step, the raw MCMB parts were carbonized in an electrical furnace with nitrogen atmosphere heated 0.5 °C/min up to 1000 °C.

2.4. Siliconization process

Siliconization operation on the porous samples was done at a high-temperature vacuum electric furnace at 1600 °C and 10^{-3} mbar. The specifications of silicon used are summarized in Table 3. The fabrication process of the C–SiC composites is shown in Fig. 2.

2.5. Characterization techniques

The density and porosity of the carbon porous preform and C–SiC composite was measured by Archimedes' method according to the ASTM C830-91 standard. The flexural

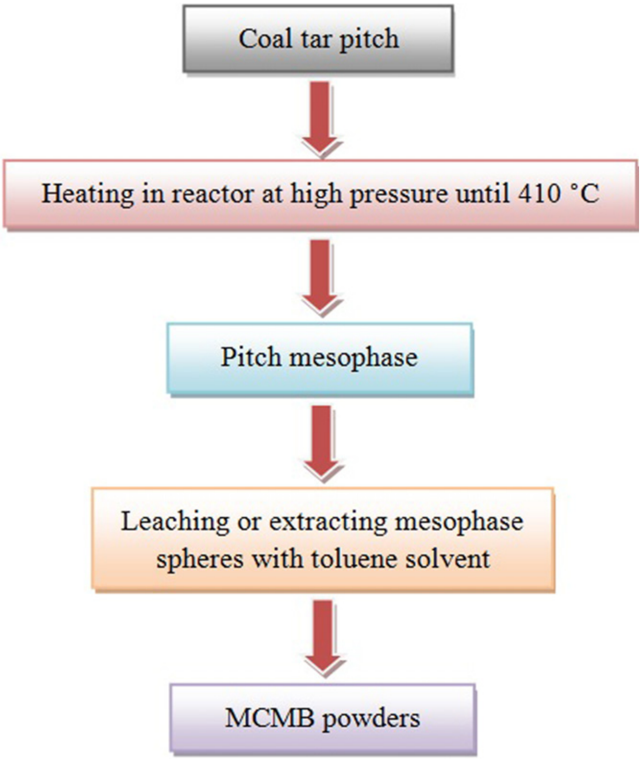

Fig. 1. MCMB fabrication from coal tar pitch.

Table 3
Chemical analysis of silicon.

%Si	%Ca	%K	%Fe	%Al
98.75	0.3	0.21	0.21	0.53

strength of the C–SiC composite was measured by three-point-bending test at room temperature on an electron universal testing machine (Gotech Universal). The dimension of the test sample was according to the ASTM C1341-97 standard. Gravimetric analysis was also applied for evaluation of the chemical analysis of the C–SiC composite. To investigate the phase analysis of C–SiC composite, the X-ray diffraction pattern was obtained through Philips pw3710 diffractometer using monochromatized Cu Kα radiation ($\lambda = 0.1540$ nm). The morphology of polished C–SiC surface was characterized by an optical microscope (OM, Kyowa, Japan) and a scanning electron microscope (SEM, Vega, Tescan, Czech).

3. Results and discussion

Fig. 3(A) shows the optical photographs of the as-received MCMBs, which are still in the matrix of heat-treated pitch. The OM and TEM micrographs in Figs. 3(B) and 4, respectively, show the morphologies of the isolated MCMBs after washing with very homogeneous size and excellent sphericity.

Table 4 lists the densities, porosities and bending strengths of the preforms before and after siliconization. During the following infiltration processing, molten Si infiltrated into the preforms and reacted with MCMBs-derived carbon to form SiC ceramics. The formed SiC and some residual Si replaced the pores in the preforms, resulting in higher densities and lower porosity of carbon preform after siliconization. A higher bending strength was obtained for siliconized samples. The variation in the bending strength is attributed to the change in the microstructure of the samples.

The crystal structure of the reaction products was investigated by X-ray diffraction. The XRD pattern of the C–SiC composite is shown in Fig. 5. The phase analysis reveals the presence of carbon, silicon carbide and unreacted silicon in this composite.

Gravimetric analysis was also applied for evaluation of chemical analysis. Unreacted silicon was removed by dissolving the composite in a mixture of 90 volume percentage nitric acid (HNO_3) and 10 volume percentage hydrofluoric acid (HF) at 40 °C for 48 h. During the dissolution, elementary silicon first oxidizes to silicon dioxide and subsequently reacts to form a stable hexa fluoro-complex according to the following equations:

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O \quad (1)$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \quad (2)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad (3)$$

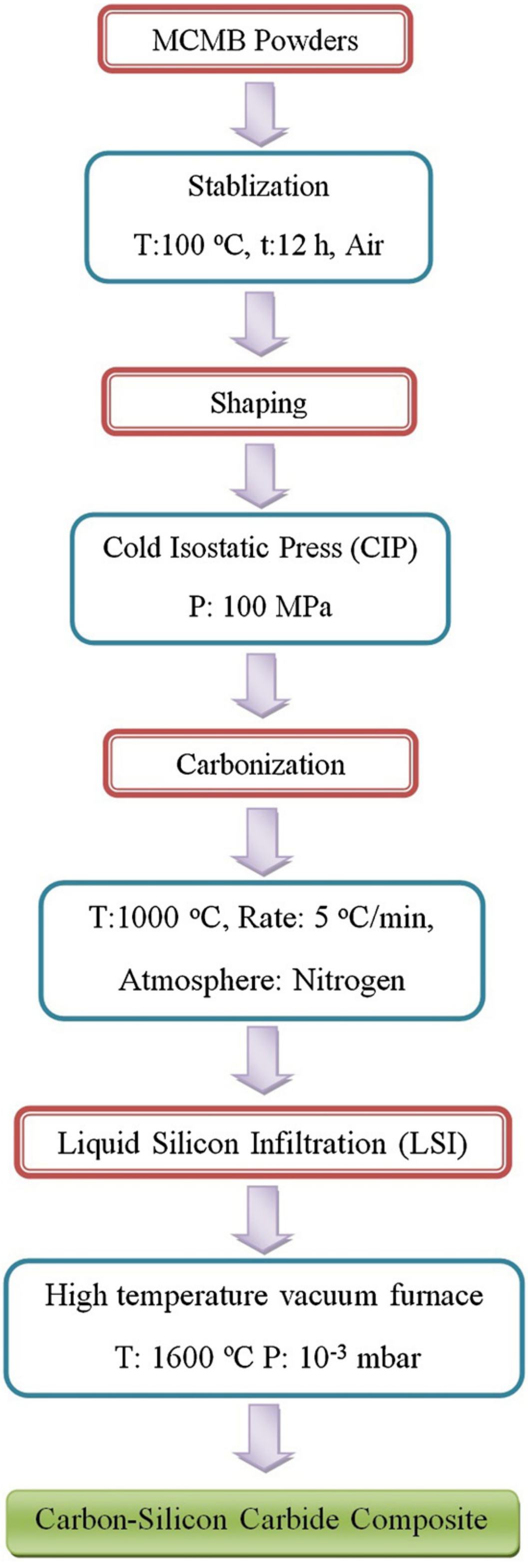

Fig. 2. Processing scheme of manufacturing C–SiC composites.

The acids only affect free silicon, whereas carbon and silicon carbide remain stable. Due to high accessibility of the SiC zones, the acid reached all the regions of residual free silicon and removed it completely. To remove the carbon completely

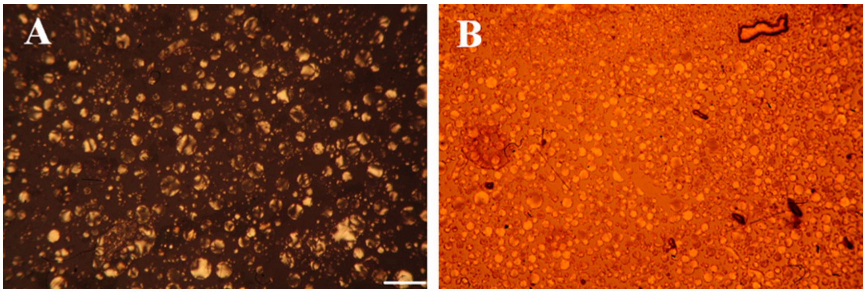

Fig. 3. (A) Optical micrographs of the mesophase pitch containing mesophase spheres. (B) Isolated MCMBs after washing.

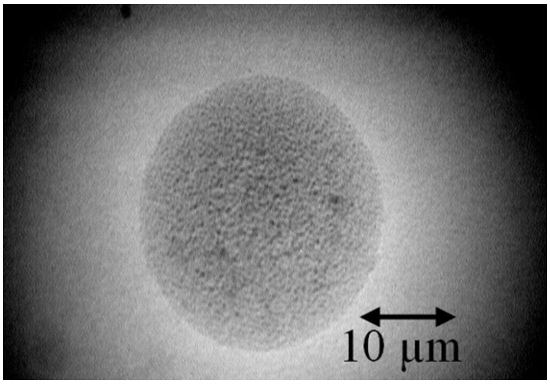

Fig. 4. TEM micrograph of isolated MCMBs after washing.

the samples were exposed to air at 700 °C for 24 h according to the following equations:

$$C + O_2 \rightarrow CO_2 \uparrow \quad (4)$$

$$2C + O_2 \rightarrow 2CO \uparrow \quad (5)$$

The content of each component can be calculated after weighing the residual mass with the result shown in Fig. 6.

The microstructural analysis revealed that there was little residual carbon but much SiC produced because of the high activity of the MCMB carbon. A large amount of SiC matrix combined with some residual silicon formed around the dense MCMB grains in the composite (Fig. 7). For porous carbon materials, silicon rapidly infiltrated the carbon preform and

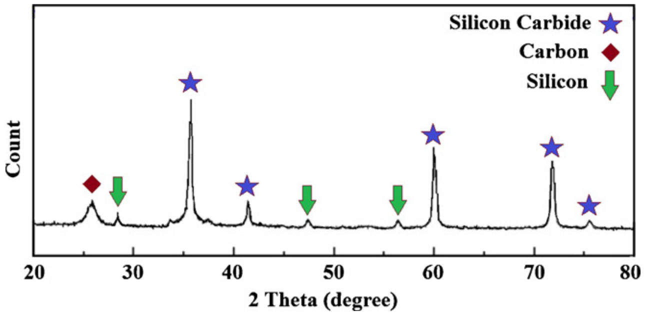

Fig. 5. XRD pattern of C–SiC composite.

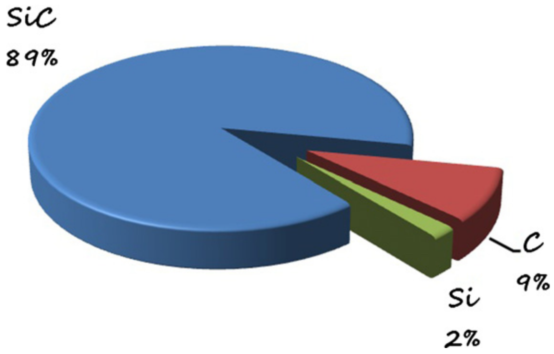

Fig. 6. Chemical analysis of C–SiC composite.

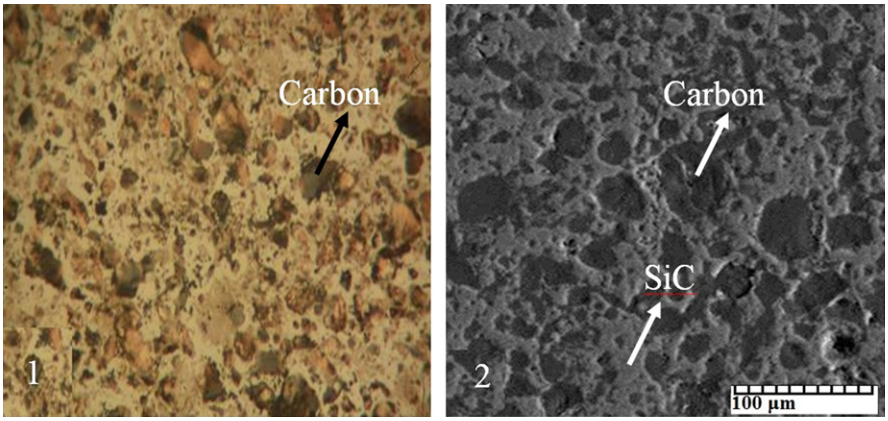

Fig. 7. Micrographs of C–SiC composite (1). Optical microscope (2). SEM microscope.

Table 4
Densities, porosities and bending strengths of carbon performs and C–SiC composites before and after siliconization.

Samples	Before siliconization			After siliconization		
	Density (g/cm^3)	Open porosity %	Bending strength (MPa)	Density (g/cm^3)	Open porosity %	Bending strength (MPa)
1	1.50	15	30	2.41	0.62	210
2	1.40	16	28	2.32	0.68	205
3	1.55	14	31	2.43	0.51	212

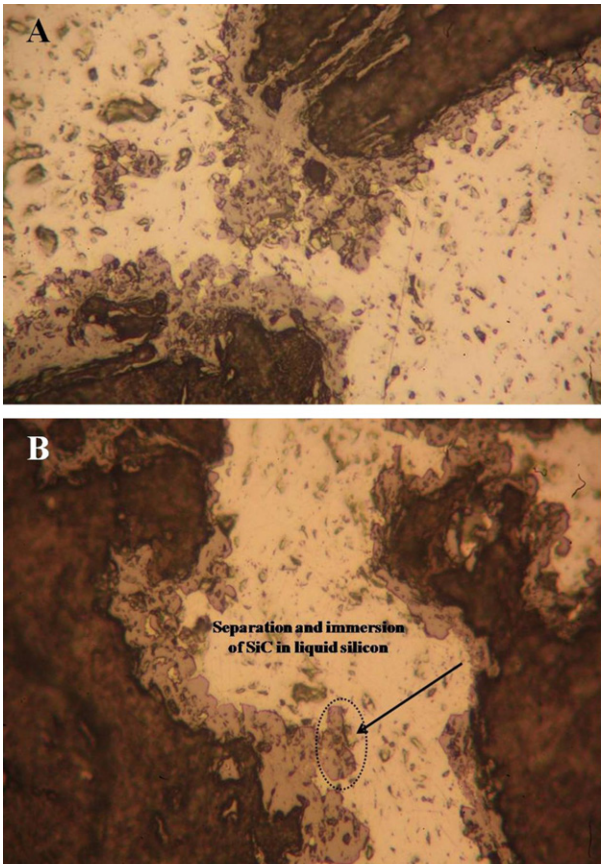

Fig. 8. Optical micrographs of C–SiC composite at the early stage of siliconization process. (A) Formation of initial SiC layer (400×). (B) Separation and immersion of SiC particle in liquid silicon (400×).

reacted with carbon form SiC during the LSI process. Hence, the macroscopic holes between the MCMB grains were filled with SiC, which also could be seen in Fig. 7.

The aim of these investigations was to obtain detailed information on the morphology of the SiC areas, the Si/SiC and C/SiC interface that might elucidate the mechanisms governing the siliconization of MCMB preforms. For this purpose, MCMB-SiC composite samples were investigated by SEM and OM. The OM and SEM micrographs of the polished cross-sections of composite in Figs. 8 and 9, respectively show the microstructure of composite at the early stage of reaction between melted silicon and carbon and at the end of siliconization process. The light brown, black and white regions in the images are identified as silicon carbide, carbon and silicon respectively (Fig. 8(A) and (B)). As can be seen from Fig. 8, after an initial reaction of carbon and molten silicon, the heterogeneous nucleation and growth of SiC occurred leads to the formation of a continuous polycrystalline SiC layer on silicon–carbon interface. The formation of this initial continuous SiC layer is very rapid and the subsequent growth is controlled by diffusion of carbon atoms and/or silicon atoms through the SiC layer. The extended contact of the reactive liquid makes the SiC layer brittle, allowing the silicon to infiltrate between the SiC crystals. The brittleness of SiC layer, higher wettability of liquid silicon on MCMBs surface and the induced stress from molten silicon are three factors lead to the separation and immersion of SiC particle in liquid silicon (Fig. 8(B)). The cross-sectional and SEM micrograph of reacted microstructure is shown in Fig. 9, which show the coarse silicon carbide crystals appeared at Si/SiC surfaces (Fig. 9(A)). Fig. 9(B) represents the interface of SiC/carbon.

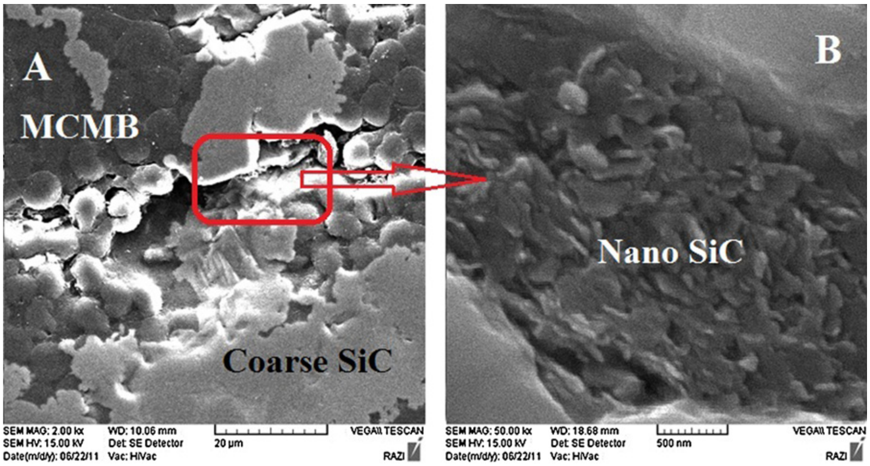

Fig. 9. SEM micrographs of C–SiC composite. (A) MCMB-coarse SiC interface. (B) Magnification of selected area.

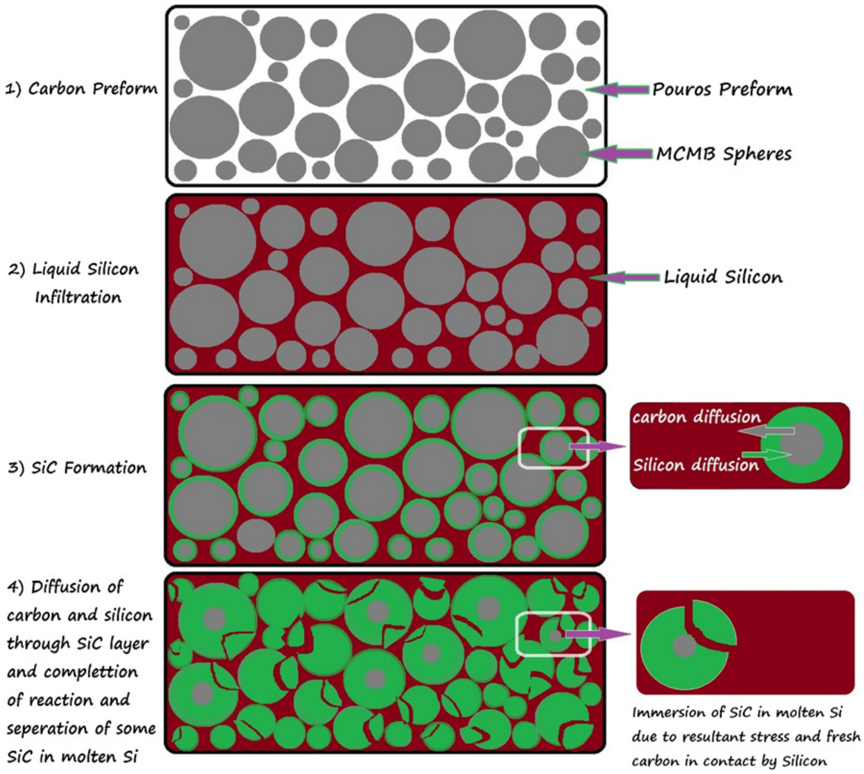

Fig. 10. Schematic model of liquid silicon infiltration of carbon porous bodies.

There are nano-SiC crystals with a mean crystal size between 50 and 200 nm. Furthermore, it seems to have been established that MCMBs are active reaction sites where siliconization leads to a steady conversion of carbon to SiC.

Based on the above analysis and the remarks of other researchers [10,16–19], a possible mechanism for fabrication of C–SiC composites via liquid silicon infiltration process is proposed, as shown in Fig. 10. The wetting angles of liquid silicon on silicon carbide and carbon are 30–45° and 0–30°, respectively. So when the melting point of silicon (1410 °C) is exceeded, silicon rapidly infiltrates the MCMB preform because of the capillary forces. The MCMB grains are hardly accessible to the silicon but the cracks and pores within the grain boundary regions could act as a communicating channel system with high capillary forces for liquids of low viscosity. These microcracks and pores within the MCMB are convenient for molten silicon to be retained and dispersed within these regions (Fig. 10(2)). Molten silicon infiltrated into the interface of MCMB spheres. In the next step in situ formation of silicon carbide was triggered, because liquid silicon rapidly wets the carbon surface [28] resulting in a spontaneous chemical reaction to SiC formation (Fig. 10(3)). Finally, a network SiC was formed and some scattered SiC particles and unreacted carbon distributed uniformly in the matrix (Fig. 10(4)).

4. Conclusions

C–SiC composites were fabricated by infiltrating molten Si into the carbon preforms derived from mesocarbon microbeads (MCMBs). It was established that the composite was composed of 89% β-SiC, 2% C and 9% Si by means of gravimetric analysis. It was found that during siliconization of MCMB preforms, SiC develops into two morphologies, a zone of coarser SiC grains between 5 and 20 μm in size at the SiC/silicon interface, and fine nano-SiC particles with dimensions of 50–200 nm at the SiC/carbon interfaces. A model of the siliconization of porous MCMB preform is proposed.

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