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High porosity SiC ceramics prepared via a process involving an SHS stage

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Abstract

The preparation of porous SiC ceramics from stoechiometric mixtures of silicon and graphite has been studied. Products with very high pore contents (≈80%) were obtained using a process which consisted of heating the reactive pellets in purified argon, at 15 °C min^{-1}, up to 1430 °C and applying a weak d.c. voltage across the sample for 20 s. The resulting electrical current was necessary for the ignition of an SHS reaction simultaneously in the whole sample. The analysis of the sample microstructure evolution all along the process has enabled the identification of the different mechanisms involved in the SiC formation. Before the SHS stage, the formation of silicon carbide, during heating from about 1325 up to 1430 °C, is associated with a large sample expansion, which mainly determined the final pore volume fraction. The pore transfer mechanisms, which occur during the SHS stage at 1430 °C, have a specific influence on the pore development. Since the final pore size distribution is strongly related to silicon grain granulometry, the porosity of the porous SiC ceramic, obtained by this process, can be easily modulated.

Keywords: Ceramics; Electrical ignition; Porosity; SHS; SiC

1. Introduction

Silicon carbide, which exhibits good mechanical properties at high temperature, significant electrical conductivity and a high melting point, is a particularly well-adapted material for applications in the domain of hot gas filtration.[1,2] However, the preparation of porous SiC based ceramics with controlled pore size is still rather expensive because it generally involves the use of starting powders with well controlled morphology, the preparation of a complex suspension and a heat treatment at high temperature ($T > 1500$ °C).

Different attempts to prepare ceramics filters via an SHS route[3,4] have already been made. This technique consists of initiating locally a very exothermic reaction within a mixture of reactive powders and to use the heat released by this reaction to obtain, in a few seconds, a complete consumption of the reactants in the whole sample.[5,6] Such simple, fast and energetically economic processes, are rather difficult to control, but lead spontaneously to very porous materials.

The heat released during the reaction between silicon and graphite is too small to lead to an SHS reaction, except when the ignition temperature is higher than the melting point of silicon (1412 °C).[7] An alternative technique, called FACS (Field Assisted Combustion Synthesis), has been proposed by MUNIR and al.[8–10] It consists of applying, at room temperature, a significant voltage across the reactive sample and to initiate locally the reaction on a surface perpendicular to the direction of the electrical current. The reaction propagates from this surface to the opposite one by the displacement of a wave.

The aim of this paper is to describe a new process which is easy to control and which avoids the formation of a layered microstructure due to unstable displacement of the propagation wave. It consists of heating progressively the sample up to a temperature slightly above that of silicon's melting point and then to promote the SHS reaction simultaneously in the whole sample (thermal explosion mode) by driving a very weak direct current through the sample. The influence of the nature and the morphology of the reactive powders on

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the electrical power necessary to obtain a complete reaction and on the final porosity of the SiC ceramic, is also reported.

2. Experimental procedure

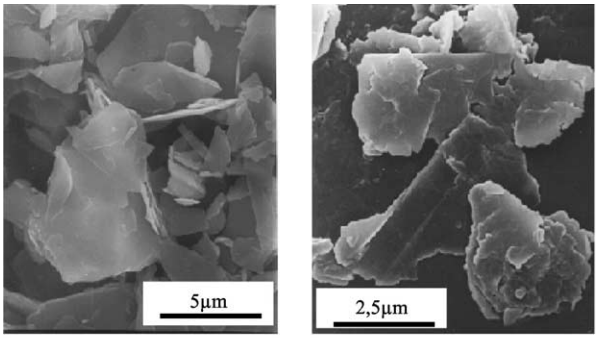
2.1. Reactive sample preparation

The characteristics of two different graphites (C Alfa, C Aldrich) and five different granulometries of the same silicon (Fluka) used in the study are given in Table 1. The platelets are isolated and very thin in the Alfa graphite and a little bit more agglomerated in the Aldrich graphite (Fig. 1). The grains of the different silicon powders, obtained after grinding and selection in an Alpine Hosokawa selector grinder, are rather equiaxed in shape.

Reactive samples are prepared from a stoechiometric ratio of graphite and silicon mixed in an ethanol/methanol solution for 30 min in an attritor. After drying, the mixtures are uniaxially pressed with a pressure ($10 < P < 30$ MPa) adapted to obtain a green relative density of $50 \pm 1\%$. The diameter and height of the as prepared reactive cylinders are, respectively, 20 and 11 mm.

2.2. Reaction conditions

A reactive cylinder is set in the middle of a tubular furnace with a continuous flow (8 l/h) of purified argon ($P_{O2} < 10^{-5}$ Pa). The vertical furnace (Pyrox VD 50) is then heated at 15 °C min^{-1}, up to 1430 °C. At this temperature, a weak d.c. voltage is applied across the sample for 20 s. The electric current is carried by two molybdenum wires (diameter 0.5 mm) from the generator to two plates of graphite (approximately 4.5 mm thickness) positioned above and below the two flat faces of the reactive sample. Two water-jackets make it possible to cool the seals and the gas supplies. The device as a whole is represented on the Fig. 2. To insure a good electrical contact between the graphite plates and the reactive sample, fine graphite powder is sprayed onto the two flat surfaces of the cylinder. The generator can supply a current from 0 to 20 A for voltages up to 30 V. The application for 20 s of an appropriate d.c. voltage leads to a thermal explosion, characteristic of an SHS reaction inside the reactive sample heated at 1430 °C.



Natural graphite
C Alfa

Synthetic graphite
C Aldrich

Fig. 1. Morphology of the graphite powders.

3. Results

The minimum current and voltage values yielding complete transformation of silicon and graphite into silicon carbide are reported in Table 2 for each type of reactive mixture.

The reaction is considered as complete when graphite and silicon peaks are no longer detected on the X-ray diffraction pattern of the powder obtained after grinding of the porous ceramic. The diffractometer used for the characterisation was an INEL CPS 120 working with Kα_1 copper radiation. The exposure time was 15 min.

The obtained porous ceramics were observed in a scanning electron microscope (Fig. 3). The three following types of SiC grains are present:

Table 1
Characteristics of the reactive powders

Nature	Specific surface area (m^2/g)	Reference	Granulometric distribution (mass%), d (µm)
Si > 30 µm[a]	0.14[b]	Fluka 97%, Fe⩽1% purity	$d_{90} = 54.2$; $d_{50} = 33.9$; $d_{10} = 23.3$
Si 20–30 µm[a]	0.17[b]		$d_{90} = 38.0$; $d_{50} = 25.7$; $d_{10} = 16.3$
Si 10–20 µm[a]	0.25[b]		$d_{90} = 24.5$; $d_{50} = 14.0$; $d_{10} = 12.3$
Si < 10 µm[a]	0.7[c]		$d_{90} = 2.5$; $d_{50} = 1.2$; $d_{10} = 0.3$
Si 1–2 µm[a]	8.6[c]		$d_{90} = 2.5$; $d_{50} = 1.2$; $d_{10} = 0.3$
Synthetic graphite	7.95[c]	Aldrich	
Natural graphite 99.9995%, purity	6.1[c]	Alfa Aesar 99.9995%, purity	

[a] Fluka silicon powder ground and selected in Alpine Hosokawa selector-grinder.

[b] Blaine specific surface area.

[c] B.E.T. specific surface area.

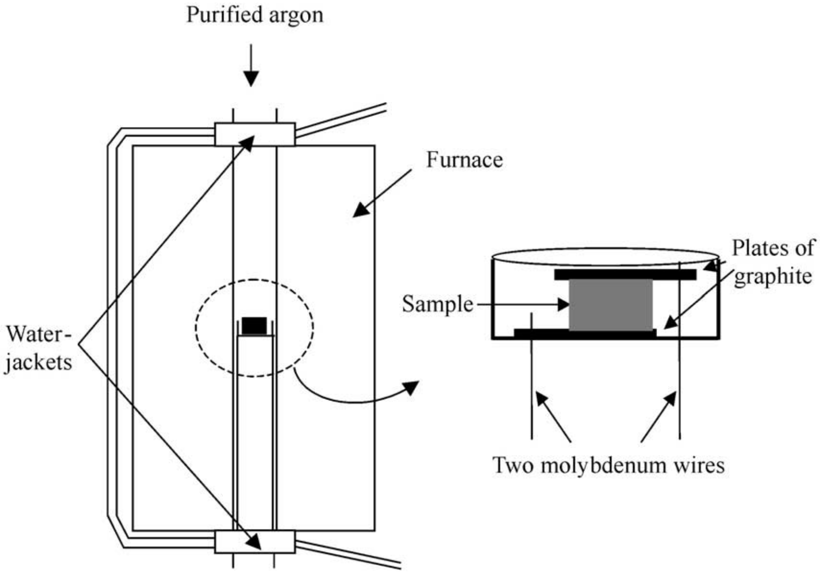
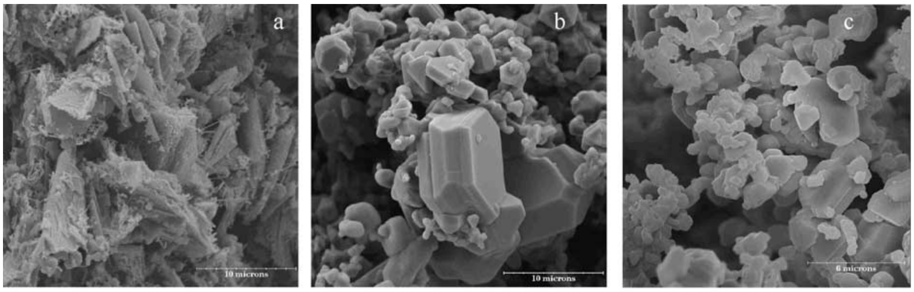


Fig. 2. Schematic of the experimental device.



C Alfa-Si 10-20µm **C Alfa-Si 20-30µm** **C Alfa-Si >30µm**

Fig. 3. Different SiC grain morphologies obtained after the SHS stage (secondary electrons).

1. very small and aggregated grains (Fig. 3a). The lamellar shape of the aggregates seems to be related to the graphite grain morphology;
2. large hexagonal grains (≈10 µm) with very regular form and smooth surfaces (Fig. 3b);
3. equiaxed aggregates of grains of intermediate size (1–5 µm) (Fig. 3c).

The open porosity has been characterized by mercury porosimetry (Autopore II Micromeritics 9200). The relative volumes of open porosity, reported in Table 3, are very high (≈80%) compared to values typically observed in commercial SiC filters (⩽60%). The pore size distribution has been calculated assuming cylindrical pores. Three examples of pore size distribution in the starting reactive sample and in the corresponding porous SiC ceramic are given in Figs. 4–6.

Table 2
Minimum current and voltage necessary to ignite the SHS stage for different types of reactive mixture and corresponding electrical power dissipation and temperature rise

Nature of the mixture	I (A)	U_{sam} (V)	W (J)	ΔT (K)
C alfa-Si > 30 µm	0.1	0.8	1.6	0.3
Si 20–30 µm	0.1	0.8	1.6	0.3
Si 10–20 µm	0.1	0.3	0.6	0.1
Si < 10 µm	0.1	14.8	29.6	5.9
Si 1–2 µm	0.1	6.3	12.6	2.5
C Aldrich-Si > 30 µm	0.1	4.8	9.6	1.9
Si 20–30 µm	0.5	4.1	41	8.1
Si 10–20 µm	0.1	6.3	12.6	2.5
Si < 10 µm	0.1	0.3	0.6	0.1
Si 1–2 µm	0.1	0.3	0.6	0.1

Table 3
Relative volume of open porosity for different SiC ceramics obtained after the SHS stage

	C Alfa	C Aldrich
Si > 30 µm	83%	79%
Si 20–30 µm	82%	77%
Si < 10 µm	80%	83%
Si 1–2 µm	78%	80%

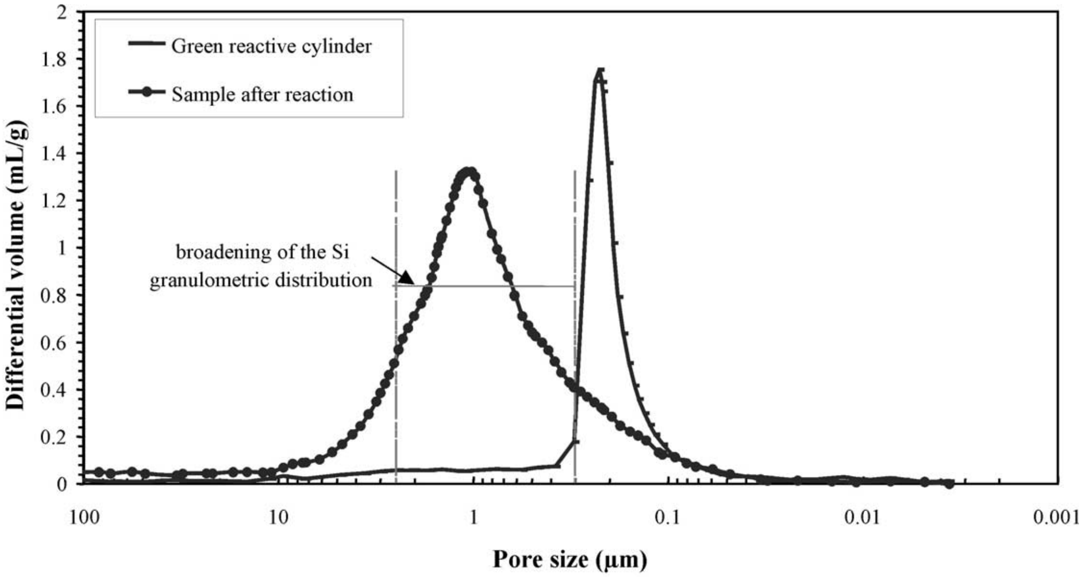


Fig. 4. Pore size distribution in C Alfa–Si 1–2 µm sample before and after reaction.

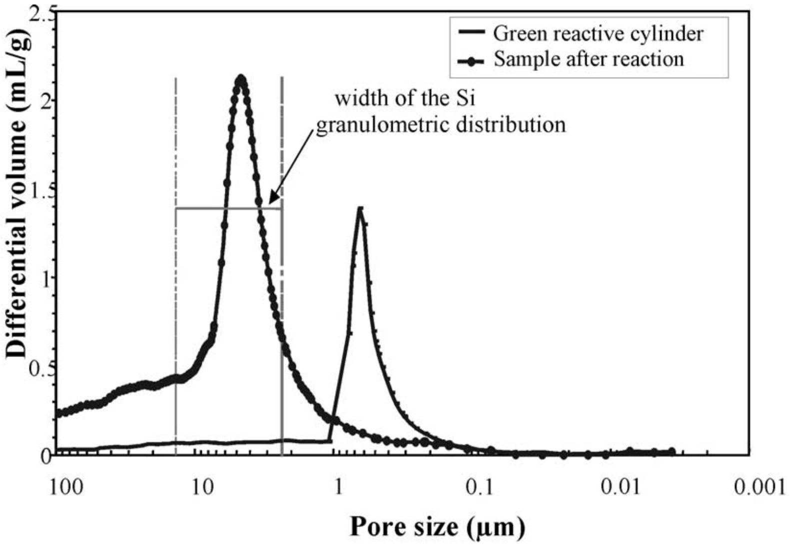


Fig. 5. Pore size distribution in C Aldrich–Si < 10 µm sample before and after reaction.

4. Discussion

4.1. Electric current effect

The influence of the electric current on the SHS reaction is obvious. Without an electric current, the total conversion into SiC is not achieved after 20 s at 1430 °C. For example, for the reactive mixture containing Si < 10 µm and C Aldrich, the observed conversion rate is 62%.

The electrical energy, W, dissipated in the sample during the 20 s of current flow through the sample is generally weak (Table 2). Assuming dissipation via the Joule effect and no heat losses, the corresponding temperature arise can be calculated from the following relation, used by Smith et al. for thermistors:[11]

$$\Delta T = \frac{W}{\rho C\text{p} V}$$

where ΔT is the average sample temperature change, V, ρ and C_p are, respectively, the sample volume, the density and the specific heat.

The calculated temperature rises, given in Table 2, are always small (< 9 °C); in half of the cases ΔT is less than 1 °C. Therefore, the electric current effect cannot be linked to a temperature increase throughout the sample, as observed by MUNIR[9] during FACS experiments. The

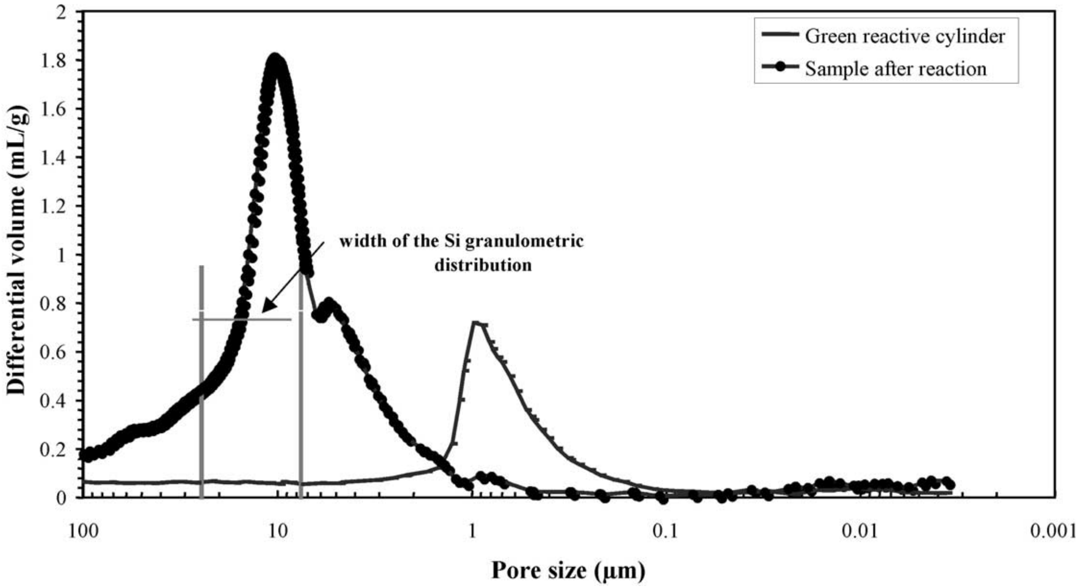


Fig. 6. Pore size distribution in C Alfa–Si 10–20 µm sample before and after reaction.

ignition of the SHS stage by such a weak electric current, could be the result of one of the following effects:

- (i) a local temperature increase at the contacts between reactive grains, which would help the spreading of silicon on the surface of graphite grains and then, the dissolution of carbon in liquid silicon;
- (ii) an activation of the migration of impurities, such as oxygen, present on the surface of the silicon grains.

Further support for argument (ii) comes from the fact that a transient thermal gradient across a 50 µm size grain should have a relaxation time which is less then a ms.[12]

4.2. Sample expansion

The sample porosity observed after reaction (Table 3) corresponds to the combination of the following three contributions:

- (i) the porosity existing in the starting reactive compact ($50\pm1\%$);
- (ii) the reduction of the volume of the solid skeleton due to the difference between the molar volumes of reactants and product. The molar volume of SiC ($V_{SiC}=12.45$ cm^3 mol^{-1}) represents 71.6% of the sum of the Si ($V_{Si}=12.05$ cm^3 mol^{-1}) and C ($V_C=5.46$ cm^3 mol^{-1}) molar volumes;[13]
- (iii) a sample expansion during reaction. Results reported in Table 4 show that the volume of all the samples increases very strongly during the process. This expansion, which was never less than 50%, even reached 90% in one case.

Table 4
Relative volume expansion (%) observed after reaction for different types of reactive samples

	C Aldrich	C Alfa
Si > 30 µm	63	78
Si 20–30 µm	55	65
Si < 10 µm	91	80
Si 1–2 µm	85	60

The reaction between silicon and carbon begins before the application of the electric current. The evolution of the conversion rate versus temperature, during heating at 15 °C/min up to 1400 °C, is given in Fig. 7 for two C Alfa based reactive mixtures. A significant amount of SiC is already formed at 1325 °C. Although no temperature rise, characteristic of an SHS process is detected below 1400 °C, the sample has already expanded. For example, at 1400 °C, the expansion of a Si > 30 µm–C Alfa based sample represents 26% of the starting volume. In this case, the main porosity formation seems not to be linked to the SHS stage.

The observation by scanning electron microscopy of a sample heated up to 1375 °C shows that SiC crystals are preferentially formed on the graphite platelet edges (Fig. 8). Such a behaviour must be correlated to the important difference of surface energy existing between prismatic and graphitic faces of graphite. As no liquid can exist at 1375 °C, the location of those crystals suggests a silicon transfer via surface diffusion on C platelets.

Sample expansion during reaction is often due to gas emission in a dense ceramic or in a liquid phase, to vacancy migration in a preferential direction (Kirkendall effect) or to coalescence of vacancies.[14] Even if

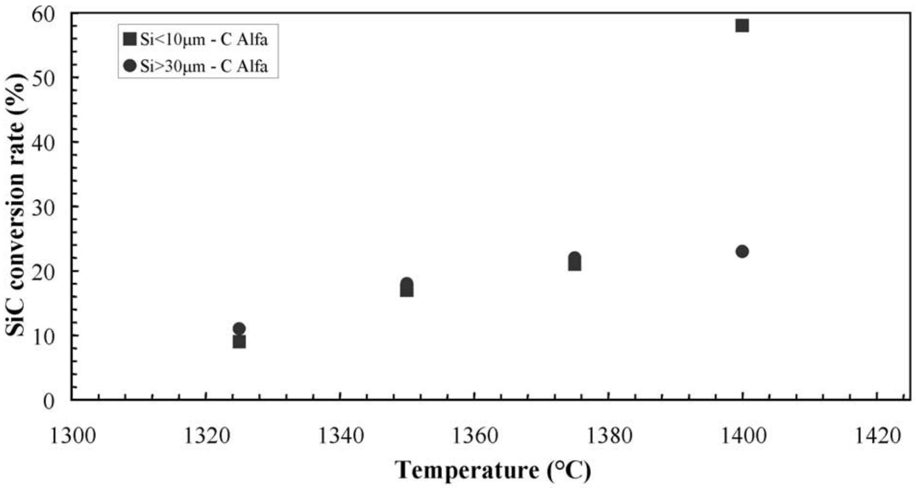


Fig. 7. Evolution with temperature of the SiC conversion rate during heating at 15 °C/min in purified argon.

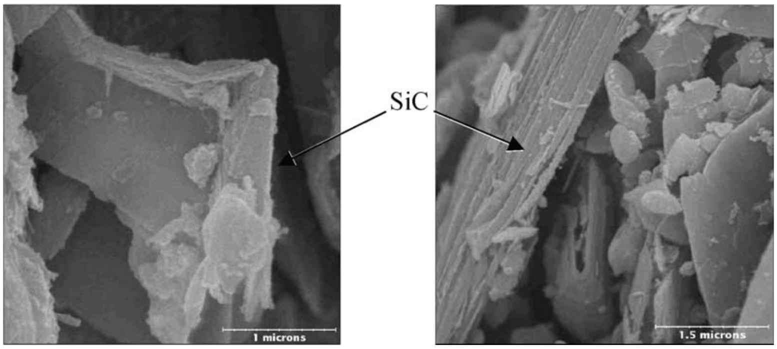


Fig. 8. Formation of SiC crystals formed on graphite platelet edges during heating at 15 °C/min up to 1375 °C (C Alfa).

these phenomena participate in the volume expansion during the reaction between C and Si, the main contribution seems to be linked to the anisotropic properties of the graphite surface. At the beginning of the reaction, the platelets, which represent about 15% of the apparent volume of the reactive sample, are rather isolated and the volume expansion is low. During this stage, the formation of SiC is compensated by the disappearance of silicon. The volume expansion occurs only when the lengthening of the platelets is high enough to lead to the formation of a continuous skeleton made of graphite partially coated with SiC. It must be noted that this progressive expansion of the sample seems to stop when the amount of formed SiC reaches about 60%. Higher conversion rates are only observed above 1400 °C in presence of a liquid phase (a eutectic exists at 1404 ± 5 °C in the Si–C system).[15] In this temperature range, the SiC formation is controlled by a dissolution/crystallisation mechanism which involves mainly the silicon based liquid.

4.3. Relation between pore and silicon grain sizes

The comparison between the width of the starting silicon granulometric distribution ($\varnothing_{10}$–$\varnothing_{90}$) and the pore size distribution (Figs. 4–6) shows that the final size of the pores tends towards that of the starting reactive silicon grains. This correlation, which is not very dependent on the graphite morphology, is less marked for large silicon grains (Fig. 6).

The results shown in Fig. 9 reveal that even if pores expand during the sample expansion, their final size is determined by the microstructure reorganisation which occurs during the SHS stage. When the electric current is applied at 1430 °C, the ignition of the SHS reaction leads to a brutal temperature increase in the sample and, then, to a strong decrease of the liquid viscosity. When the liquid spreads very quickly onto the graphite platelets, the volume of space occupied by the silicon is left empty, generating the pores of the final product. If the temperature reached during the SHS stage is higher, this mechanism is reinforced

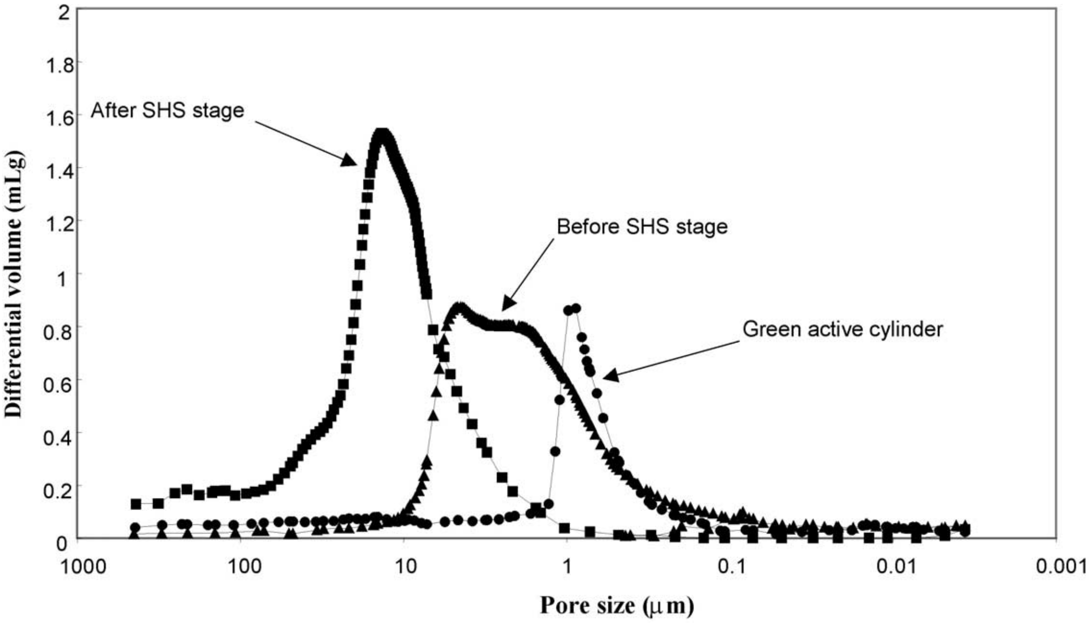


Fig. 9. Evolution of the pore size distribution along the process (C Alfa–Si 10–20 µm type sample).

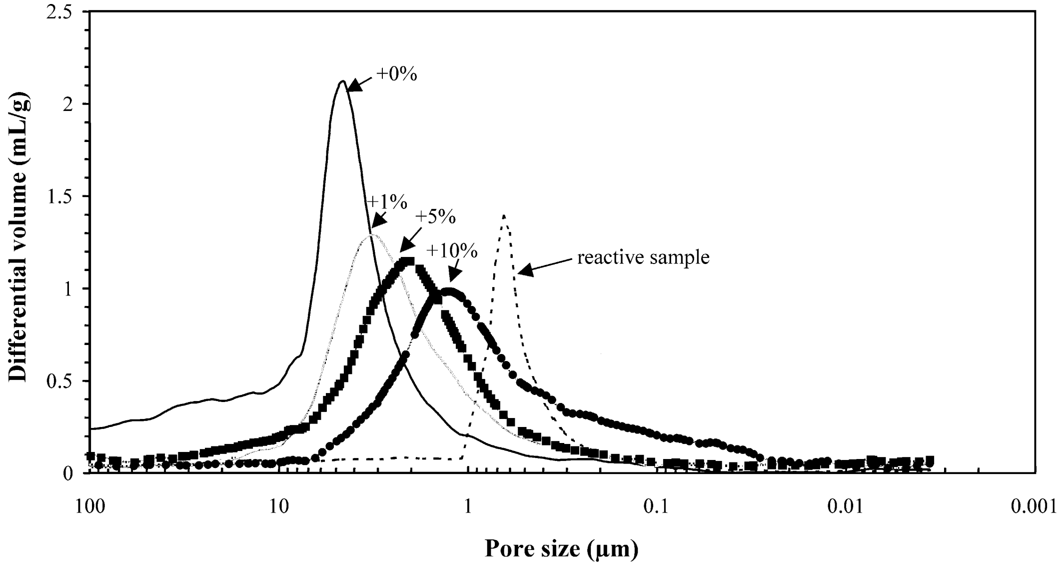


Fig. 10. Influence of the amount (wt.%) of SiC added in the reactive mixture on the pore size distribution in the obtained ceramic after the SHS reaction.

because of the consequent decrease of viscosity. For example, the addition of SiC grains to the reactive sample, which dilutes the reaction, reduces the maximum temperature reached during the process and also the pore size in the final ceramic (Fig. 10). We have observed that the pores become smaller and smaller as the amount of SiC in the starting mixture is increased.

5. Conclusion

Porous SiC ceramics can be obtained by heating, in purified argon, a stoechiometric mixture of silicon grains and graphite platelets at 15 °C/min up to 1430 °C and by applying for 20 s at this temperature a very weak d.c. voltage. Even if the electrical energy dissipated in the sample is very weak, often less than 2 J, this latter step is necessary to ignite the SHS reaction between Si and C. During heating, the formation of silicon carbide, which occurs on the edge of the graphite platelets, is associated with a strong expansion of the sample. The relative porosity of the final porous ceramics, slightly enhanced during the SHS stage, is about 80%. The porous materials prepared using this procedure exhibit a pore size distribution which is strongly linked to the granulometry of the reactive silicon powder used.

The porous ceramics, obtained with the process described in this paper, present more open porosity than commercial SiC filters of similar pore size. However, their resistance to degradation in time must be improved.

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