

PREPARATION OF RBSC FROM PETROLEUM RESIDUES BY REACTIVE INFILTRATION WITH LIQUID SILICON

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Abstract

Reaction Bonded Silicon Carbide (RBSC) has been prepared by reactive infiltration of porous carbon preforms with liquid silicon. Porous carbon preforms have been produced by conformation and heat treatment of self-sintering petroleum semicoke powder. The effect of the petroleum feedstock and pyrolysis conditions on the sinterability of the powder to produce carbon preforms suitable for infiltration as well as the reactivity of the different carbons with silicon to produce RBSC were studied.

Introduction

Silicon carbide advanced ceramics are leading candidate materials for a wide range of structural applications, particularly at high temperature, in aeronautics, energy, electronics, nuclear and transportation industries (Wang 2004). Reaction Bonded Silicon Carbide (RBSC) fabrication is a liquid-solid reaction process which involves a rapid transformation of a porous carbon preform into a SiC body by reactive infiltration with liquid silicon (Moon 2001). However, successful development of this technique requires understanding of the various steps involved in the process, namely, i) fabrication of the carbon preforms, ii) infiltration with liquid silicon and iii) chemical reaction to convert carbon into silicon carbide (Sangsuwan 2001). The process for fabricating carbon preforms is well developed. Porous carbon preforms of different microstructures (pore size and pore volume fraction) can be produced by several methods. The most common methods are: i) pyrolysis of a solid resin obtained by polymerization of a mixture of furfuryl resin, furfuryl alcohol, diethyleneglycol, triethyleneglycol and para-toluene sulfonic acid (Chiang 1991; Hozer 1995; Hozer 1996); and ii) pyrolysis of a preform obtained by molding of a mixture of SiC and carbon particles bound by phenolic resin as binder (Ness 1986; Whitehead 1992). The porous microstructure is obtained by thermal degradation of the organic compounds and it can be controlled by varying the ratio of the mixture components and heat treatment conditions.

However, in recent decades, a wide variety of carbon materials (green coke, needle coke, delayed coke, etc.) have been developed from petroleum residues, suitable for production of carbon artefacts (anodes, electrodes, crucibles, etc.) (Marsh 1997; Mochida 1994). During pyrolysis, petroleum pitch undergo inter and intra molecular reactions with molecular growth to form solid cokes via the deformable, plastic or fluid semicoke (Lewis 1982). Semicokes are constituted by two main different phases: an anisotropic phase called mesophase and an isotropic matrix. Mesophase is formed by lamellar arrangement of aromatic molecules in parallel layers while the isotropic phase is less ordered. The isotropic phase is more plastic, deformable and fusible (Marsh 1999). Semicoke powders are self-sinterable materials due to their plasticity. Since the composition of mesophase powders can control the fusibility of the material upon pyrolysis, the nature of the starting material and the applied pyrolysis conditions to obtain the semicokes are very important to determine the porosity and microstructure of the carbon materials (Martinez-Escandell 1999), which may play a great role in the infiltration process and the reaction with silicon.

The aim of the present study is the production of semicoke powders from petroleum residues with optimum self-sinterability to conform carbon preforms without addition of binder. After carbonization, carbon preforms must have an adequate porous microstructure allowing for a successful infiltration with liquid silicon to produce RBSC. Reactive infiltration process is controlled by both the porous microstructure and the reactivity of the carbon material with silicon. Therefore, carbon preforms of a wide range of porosity were prepared by varying the pyrolysis parameters (temperature, time) and the conformation pressure. The reactivity of the carbon material with silicon was controlled using three different petroleum residues.

Experimental procedure

Material used

Three different petroleum residues have been used as feedstock in this work. Ethylene-tar (PY), the most aromatic, a decant oil (DO), intermediate, and a vacuum residues (VR) of lower aromaticity and higher ramified hydrocarbons.

Experimental methods

Pyrolysis process of the feedstocks was carried out into a laboratory pilot plant. The special features of this system include a maximum sample capacity of 1000 cm³ and an ability to work under pressure. Heating of the reaction tube occurred in a preheated fluidised sand-bath furnace. Heating rates were constant at 15°C/min. The reactor tube was made

of Pyrex glass, 65 mm diameter, 210 mm height and containing 350 g of feedstock. The tube was placed within the steel block which was within the sand bath (to ensure a maximum uniformity of temperature). All pyrolyses were carried out under an atmosphere of nitrogen, (99.999% pure), the nitrogen also being used to establish the working pressure of 1 MPa in the system. In order to have a wide range of pyrolysis conditions (at constant heating rate), variations were introduced into the maximum pyrolysis temperature 440–480°C and soak time 0–6 hours, in various combinations. The system was depressurised at reaction temperature at the end of each experiment, causing a second distillation, and then cooled down to room temperature.

The solid semicoke obtained was ground using a ball mill to obtain the semicoke powder. The powder was classified as a function of the particle size using a sieve shaker and the fraction of particles with diameter below 63µm was selected for the conformation of the semicoke preforms. Conforming of the carbon preforms was carried out by uniaxial pressing of the semicoke powders during 1 minute at different pressing pressures, depending on the self-sintering properties of the material. Semicoke preforms were heated up to 1400°C during 60 minutes into a horizontal tube furnace using a heating ramp of 1°C/min and a flowing argon atmosphere of 60ml/min. Subsequently, the porous carbon preforms were infiltrated with liquid silicon in order to obtain the RBSC material. For the infiltration step, porous carbon preforms were placed into an alumina crucible and solid silicon pieces were put on top. Silicon was added with a 10wt% in excess. The materials were heat treated up to 1450°C during 180 minutes into a horizontal tube furnace using a flowing argon atmosphere of 60ml/min.

Characterization of the raw semicokes

Optical Microscopy

Semicokes as obtained from the pyrolysis reactor were mounted into a cold setting epoxy resin. The polished surface was examined by optical microscopy using reflected polarised light. Quantitative assessment of content in isotropic and anisotropic phase (spheres and anisotropic domains) was assessed using a point-counting technique based on analysing 25 fields from a total of 2500 counted points.

Solvent solubility

The insolubility in toluene of the semicokes was determined using a standard procedure (STPTC S. No. RT 8-62). The procedure to determine the insolubility in 1-methyl-2-pyrrolidone (NMP) is as follows: 1g of sample (<0.5mm particle diameter), and 25ml of NMP were placed in a 100ml flask, heated to boiling point and kept under reflux for 30 min. The solution was filtered and the residue washed in steps with hot NMP, toluene and acetone.

Volatile Matter

The volatile matter content of semicokes was determined using the following procedure: 1g of dry sample was placed into a crucible and heat treated up to 900°C using a rate of 5°C/min, and kept at that temperature for 30min in a flowing nitrogen atmosphere of 60ml/min. The results are expressed as wt% of lost material.

FTIR

Aromaticity of the semicokes was analysed by DRIFT, Mattson Infinity Gold FTIR. Areas of absorption corresponding to C-Har vibrations (2990-3150cm⁻¹) and C-Hal (2800-2990cm⁻¹) were obtained. The aromaticity parameter (C-Har/C-Hal) was calculated as the ratio of the two areas.

Softening Point

Softening Point of semicokes was determined using a Thermomechanical Analyzer 2940 from TA Instruments. 0.15g of the ground semicoke (particle size <500µm) were heat treated under 150ml/min of nitrogen flow at 5°C/min, using an expansion probe and a force of 0.05N.

X-Ray Diffraction

The X-ray diffraction pattern of the semicoke powders after pyrolysis and after carbonization up to 1500°C were obtained in a Bruker model D8 Advanced diffraction system, equipped with a Cu cathode and Ni filter. Monochromated Cu K α radiation ($\lambda=1.5406\text{\AA}$) was used. The device operated at 40kV and 40mA and for the measurement a step of 0.1° and a preset time of 3s were used in the angular scanning from 10 to 80°.

Characterization of the heat treated preforms

Physical Characterization

Bulk density and open porosity after heat treatment up to 1400°C during 60 min were measured using the DIN 51918 standard tests.

Characterization of the produced RBSC

Physical Characterization

Bulk density and open porosity of the RBSC artefacts produced by reactive infiltration of the porous carbon preforms with liquid silicon at 1450°C during 180 min were measured using the DIN 51918 standard tests.

X-ray diffraction

The crystalline structure of reaction products was determined by X-Ray Diffraction (XRD) using an X-Ray diffractometer Bruker model D8 Advance equipped with a Cu cathode and Ni filter. Monochromated Cu K α radiation ($\lambda=1.5406\text{\AA}$) was used. The device operated at 40kV and 40mA and for the measurement a step of 0.1° and a preset time of 3s were used in the angular scanning from 10 to 80° . To overcome the non-planarity of the samples a Göbel mirror was used in order to work properly with parallel optical beam.

Optical Microscopy

RBSC artefacts were sectioned using a slow cutting saw ISOMET from Buehler with diamond wafer 15LC. The cross sections were embedded into diallylphthalate resin and the surface was polished following proper metallographic techniques. The microstructure of the RBSC artefacts produced from semicoke powders was examined by optical microscopy using an optical microscope PM3 from Olympus.

Result and Discussion

Characterization of the raw semicokes.

Both composition of petroleum residue and pyrolysis conditions control the rate of development and the structure of mesophase. The reactivity of the petroleum residue constituents modifies viscosity during pyrolysis and thus the microstructure of the resultant semicokes and cokes. The deformability of the semicoke powder upon conforming pressure and its thermofusibility during heat-treatment is going to be a consequence of the composition and mesophase structure of these semicokes (Martinez-Escandell 2002). Table 1 presents a summary of the characterization of the semicoke powders. The insolubility of the semicokes in toluene (TI) and NMP (NMPI) are presented in the form of yield of solid material after extraction. Very little variation is obtained in TI, while larger differences are observed in NMPI and β -resins content. These two parameters give an idea of the amount of heavy fraction and binder phase, respectively, indicating that the heavy fraction is lower in DO, but larger the binder phase. β -resins content is defined here as the difference between TI and NMPI. Aromaticity of the semicokes powders was calculated as the ratio between the areas corresponding to aromatic and aliphatic hydrogen-carbon bonds. The most aromatic semicoke is that obtained from PY, followed by the one obtained from DO and finally the obtained from VR. Small differences are observed in the amount of volatile matter between semicokes.

Table 1. Characterization of semicoke powders. T: maximum pyrolysis temperature; t: Soak time during pyrolysis; TI:Toluene insoluble matter; NMPI: 1-methyl-2-pyrrolidone insoluble matter; CHar/CHal: ratio between aromatic C-H bonds and aliphatic C-H bonds. Volatile: volatile matter; Tsoftening: Softening point of the semicoke.

Semicoke	T ($^\circ\text{C}$)	t (h)	TI (wt%)	NMPI (wt%)	β -resin (wt%)	CHar/CHal	Volatile (%)	Tsoftening ($^\circ\text{C}$)
VR	460	3	97	94	3	0,9	11,0	400
PY	480	5	96	94	2	8,3	8,7	325
DO	480	6	98	85	13	7,1	11,0	300

Figure 1 exhibits the microstructure of the semicoke produced from every feedstock. It is quite evident that the development and distribution of mesophase is completely different for each precursor.

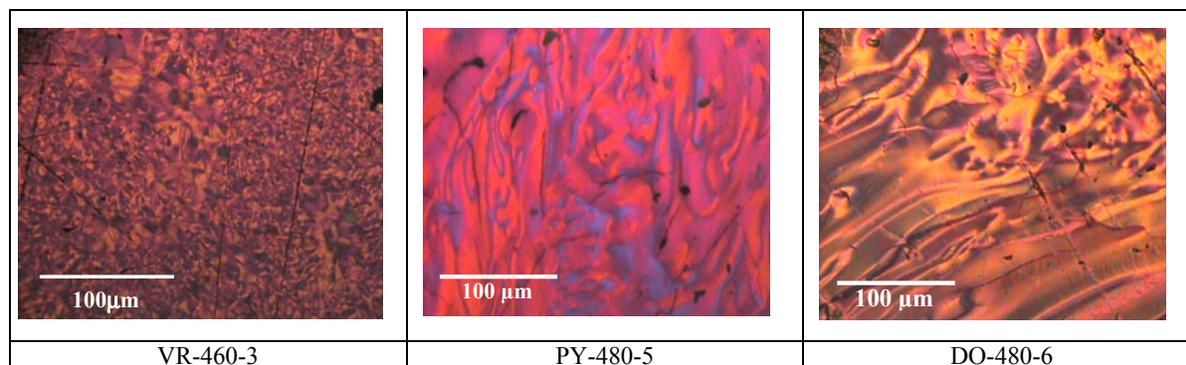


Figure 1. Optical micrographs of the semicokes produced after pyrolysis from the different petroleum residues

VR is the most aliphatic and ramified residue and hence, the most reactive during pyrolysis. Thus, semicoke produced from VR exhibits a mosaic microstructure. The ability to graphitize of any carbon material is thus predetermined entirely by the size of mesophase structures of the bulk mesophase. The smaller the mesophase structures of the initial bulk mesophase, the smaller the final degree of graphitization reached (Oberlin 1984). Therefore, the yield

of coke obtained from VR is low and the coke is of poor quality, with lower crystallinity. On the contrary, PY is the most aromatic material, the viscosity is low and the mobility of mesophase spheres is higher, thus favouring their coalescence to form larger graphitic domains typical for flow anisotropy optical texture. DO is more aliphatic than PY but with molecules that are hydrogen donors that stabilize the free radicals formed during pyrolysis, thus decreasing the rate of polymerization and keeping lower viscosity during higher temperatures. This is the less reactive material during pyrolysis and leads to the most ordered coke formed by flow domains. Percentage contents of isotropic and anisotropic phase of the semicokes were quantified optical micrographs. The content of each phase for every material is given in Table 2. The results are quite similar for the three materials. The structure of the mesophase may play an important role upon the reactivity with silicon (Narciso-Romero 1999) and a different behaviour is to be expected for each semicoke.

Table 2. Percentage content of isotropic and anisotropic phase of the semicoke obtained by analysis of the optical micrographs.

Semicoke	T (°C)	t (h)	Isotropic (%)	Mesophase	
				Coalesced (%)	Spheres (%)
VR	460	3	1	99	0
PY	480	5	1	99	0
DO	480	6	2	98	0

Fabrication of porous preforms

As mentioned above, reactive infiltration process is limited by two factors: the porosity of the material to infiltrate and the reactivity of the material with silicon. To study the influence of preform porosity in the infiltration process, carbon preforms with different porosity volume fraction were fabricated. PY was selected as raw material for the production of semicoke powder to conform these preforms, as it exhibits intermediate mesophase structures between VR and DO. It is supposed also to have an intermediate compactability in the powders, and also an intermediate fusibility. Forming pressure must be optimised to give an adequate porous structure to carry out the infiltration process. The amount of porosity is going to depend on the applied pressure upon sintering, but also in the fusibility of the powders upon pyrolysis. Once determined the optimum porosity for the semicoke obtained with PY, forming pressure would be optimised for DO and VR semicokes to obtain similar porosity development.

PY was pyrolyzed at different conditions between 460-480°C and 1-6 hours. Semicokes were ground and classified. The particle fraction with diameter below 63µm was selected for the conformation of the preform. Semicoke preforms were heat treated up to 1400°C during 60min using a heating rate of 1°C/min. During heat treatment up to 1400°C the volatile matter must be released, the lighter matter decomposed, and anisotropic phase undergoes structural changes due to the growth of the graphene layer forming distorted and wrinkled layers that appear below 2000°C (Oberlin 1984). All these phenomena develop a porous network into the carbon preform that will be used to perform the infiltration. The semicoke preforms conformed with powders pyrolyzed less than 3hours at 480°C, swelled during heat treatment up to 1400°C during 60min. Table 3 shows the density and porosity of samples that did not swell during heat treatment. Porous carbon preforms in a range of porosity from 14-36% were fabricated.

Table 3. Preparation conditions, density and porosity of the porous preforms after heat treatment at 1400°C stable dimensionally and the RBSC produced from PY. T: maximum pyrolysis temperature; t: Soak time during pyrolysis; P: conforming pressure applied during 1 minute; ρ_g : geometrical density; Popen: open porosity measured by impregnation with water.

Sample	Pyrolysis		Conforming P (MPa)	Carbonized 1400°C	
	T (°C)	t (hours)		ρ_g (g/ cm ³)	P _{open} (%)
PY-480-3-160	480	3	160	1,64	15
PY-480-3-200	480	3	200	1,67	14
PY-480-3-240	480	3	240	1,70	15
PY-480-4-160	480	4	160	1,34	32
PY-480-4-200	480	4	200	1,36	31
PY-480-4-240	480	4	240	1,39	30
PY-480-5-160	480	5	160	1,28	36
PY-480-5-200	480	5	200	1,31	34
PY-480-5-240	480	5	240	1,33	33
PY-480-6-200	480	6	200	1,43	31
PY-480-6-240	480	6	240	1,42	29

Fabrication of RBSC

All the porous carbon preforms that kept dimensionally stable during heating up to 1400°C were infiltrated with liquid silicon at 1450°C during 180 minutes. Only in one case, the infiltration process was performed completely across the piece producing a RBSC artefact with a density of 2.6g/cm³ and an open porosity of 2.4%. This fact occurred when using the preforms with the largest porosity (36%). The rest of the infiltrated preforms showed an unreacted carbon core. The chemical composition of the reaction products was confirmed by X-ray diffraction and Figure 2 exhibits the XRD spectra for RBSC material. The peaks corresponding to β -SiC produced from chemical reaction between carbon and silicon and additional small peaks corresponding to residual Si and carbon remaining after reaction are clearly showed.

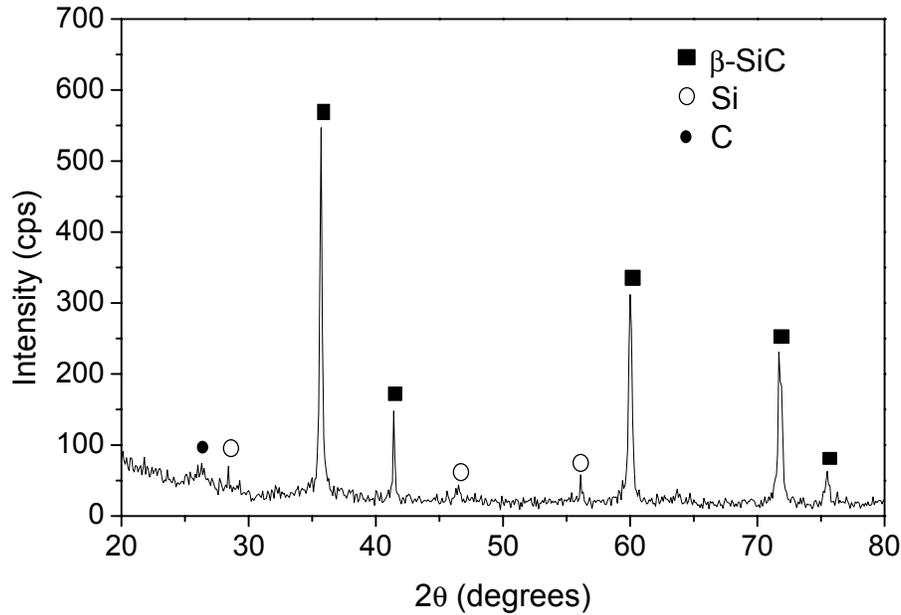


Figure 2. XRD pattern of RBSC produced from the porous carbon preforms PY-480-5-160.

The infiltrated sample was cut off and the cross section embedded in a thermosetting resin and polished properly. The microstructure of the RBSC produced was observed by optical microscopy. Figure 3 shows the optical micrograph corresponding to the centre of the RBSC artefact. Three different phases can be observed. The RBSC is composed by a dense β -SiC structure with a relatively high content of unreacted carbon and some close porosity (the β -SiC that is the coloured part, unreacted carbon zones with light grey and orange colour and close porosity in black). These results match the data measured by DRX.



Figure 3. Optical micrograph of the RBSC material produced from PY-480-5-160. Image taken using polarized light.

Effect of carbon reactivity

The effect of carbon reactivity with silicon to produce RBSC was studied using semicokes derived from feedstocks with different chemical composition. Similarly to the PY case, a wide range of porous carbon preforms were fabricated with VR and DO. For porous carbon preform produced from PY the infiltration process was only carried out completely for the preform containing a porosity of 36% volume fraction. Therefore, only those carbon preforms with porosity values higher than 36% were selected for infiltration with liquid silicon. Porosity volume fraction is a critical factor affecting the development of reactive infiltration process.

As indicated above, VR has a faster polymerization rate than PY. Thus, VR was pyrolyzed at lower temperatures between 440-460°C and shorter soak times 1-3h in order to obtain deformable semicoke powders. VR semicoke preforms were carbonized up to 1400°C during 60 min. Analogously, porous carbon preforms were infiltrated with silicon and characterized. Table 4 shows the properties of RBSC material produced from vacuum residue. For VR derived carbon preforms, the infiltration was complete only for preforms with porosity content higher than 40%. Despite of the complete infiltration of the preform, not all carbon was converted into SiC and carbon areas were observed in the cross section of pieces. It seems that reaction has not been completed due to the lower reactivity of the VR-semicoke with silicon.

Table 4. Preparation conditions, density and porosity of the porous preforms after heat treatment at 1400°C with porosity higher than 36% and the RBSC produced from VR. T: maximum pyrolysis temperature; t: Soak time during pyrolysis; P: conforming pressure applied during 1 minute; ρ_g : geometrical density; Popen: open porosity measured by impregnation with water.

Sample	Pyrolysis		Conforming	Carbonized 1400°C		RBSC	
	T	t	P	ρ_g	P_{open}	ρ_g	P_{open}
	(°C)	(hours)	(MPa)	(g/cm ³)	(%)	(g/cm ³)	(%)
VR 460-3-20	460	3	20	1,20	41	2,56	10
VR 460-3-30	460	3	30	1,24	39	2,37	16
VR 460-3-40	460	3	40	1,28	38	2,24	20

DO followed the same pyrolysis procedure than PY. In conformation process, lower pressures were applied due to the higher sinterability and plasticity of this semicoke as consequence of the higher content in β -resin. Table 5 summarizes the preparation conditions of these preforms and their density and porosity values. For DO derived carbon preforms, the infiltration was carried successfully in preforms containing a porosity volume fraction higher than 40%. A higher conversion degree of carbon into SiC was observed for this material. In Figure 4, corresponding to the XRD pattern of the RBSC produced from DO semicokes, higher development of β -SiC peaks can be observed as well as a lower content of residual silicon and carbon in the RBSC artefact. Higher reactant consumption due to higher reactivity between DO carbon and silicon are observed. Additionally, the unreacted carbon content into the RBSC was lower than for the other materials. Thus, using the optimum porosity to carry out the infiltration, larger densities and lower open porosities are achieved in the RBSC artefacts prepared from DO semicokes.

Table 5. Preparation conditions, density and porosity of the porous preforms after heat treatment at 1400°C with porosity higher than 36% and the RBSC produced from DO. T: maximum pyrolysis temperature; t: Soak time during pyrolysis; P: conforming pressure applied during 1 minute; ρ_g : geometrical density; Popen: open porosity measured by impregnation with water.

Sample	Pyrolysis		Conforming	Carbonized 1400°C		RBSC	
	T	t	P	ρ_g	P_{open}	ρ_g	P_{open}
	(°C)	(hours)	(MPa)	(g/cm ³)	(%)	(g/cm ³)	(%)
DO 480-6-20	480	6	20	1,16	42	2,73	3
DO 480-6-30	480	6	30	1,21	41	2,70	5
DO 480-6-40	480	6	40	1,25	39	2,47	14

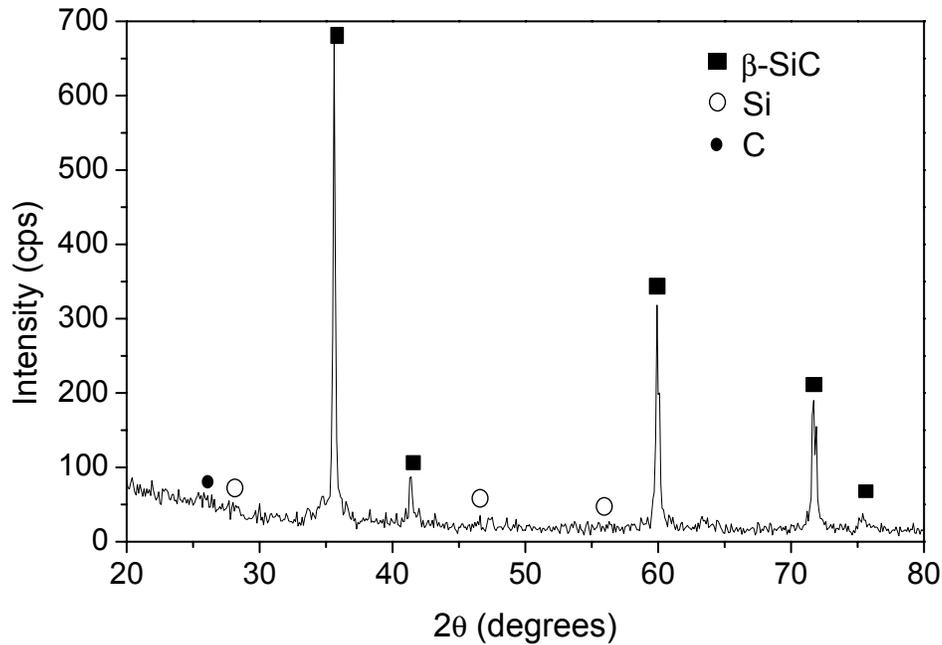


Figure 4. XRD pattern of RBSC produced from the porous carbon preforms PY-480-5-160.

To sum up, it seems that the different reactivity of carbon derived from these petroleum residues with silicon to form SiC can be attributed to the different structural organization, when comparing samples of adequate porosity to carry out the infiltration, the more ordered one being more reactive (Narciso-Romero 1999).

Conclusion

A wide range of carbon preforms were conformed from different semicokes without addition of a binder. Some of them, after heat treatment up to 1400°C during 60 minutes were stable dimensionally and showed a porous structure suitable for infiltration. Only the preforms that have porosity above 35% were completely infiltrated. In the rest of the cases, the infiltration was stopped due to blocking of the infiltration front. The degree of conversion of carbon into SiC depends on the reactivity of the carbon substrate with silicon, being higher for the more ordered carbon substrate.

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