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Nano-SiC implantation into the structure of carbon/graphite materials made by pyrolysis (carbonization) of the precursor system coal tar pitch/poly(dimethylsiloxane)

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Abstract

Conversion of the air-cured poly(dimethylsiloxane) $\{-O-Si(CH_3)_2-\}_n$ to SiC during co-pyrolysis with a coal tar pitch is studied with reference to the related SiO₂/pitch system. Each binary mixture is first homogenized at 160 °C followed by carbonization at 500 °C under argon to afford initial carbonizates. In both cases, one part of the initial carbonizate is further pyrolyzed at 1300 °C and another part at 1650 °C under an argon flow resulting in composite products. All products are studied with FT-IR, XRD, and XPS spectroscopic methods supplemented with SEM and 'wet' Si-analyses, when applicable. Carbothermally assisted conversion of both silicon precursors to nanocrystalline SiC embedded in the evolving C-matrix, i.e. nano-SiC/C composites, is evident only after the 1650 °C carbonization stage. © 2003 Elsevier Ltd. All rights reserved.

1. Introduction

Many modern applications of carbon/graphite materials force upon manufacturers significant improvements of specific materials properties which, in many cases, are attainable only by use of additives (modifiers). One of such modifiers is silicon that upon introducing to raw carbon materials in the form of various compounds is eventually converted to the advantageous silicon carbide, SiC. The standard way to achieve such a goal is to add a silicon precursor to a raw materials mixture. In the subsequent carbonization stage, conversion of the precursor takes place concurrently with the evolution of carbon matrix. Coal tar pitches are commonly used as binders in such precursor systems and constituting their most reactive component [1]. That is why investigations of co-pyrolysis of a pitch with silicon precursors are at the core of understanding the limiting processes leading there to the formation of SiC.

There are a few reports available on pitch modifications with silicon compounds specifically aimed at improved carbon materials [2]. One of the examples includes a study on a pitch modified with tetraethylsilicate leading to SiC/graphite composites [2a]. In this case, the beginning of SiC formation was observed already after pyrolysis at 1000 °C

followed at higher temperatures by partial 'oxidation' of SiC with oxygen present in the system. The formation of the transient Si–O–C species hampered an efficient conversion to SiC that could only be accomplished at temperatures above 1440 °C resulting in β-SiC whiskers. In another work, a petroleum pitch has been treated with trimethylsilyl chloride or dimethylaluminium chloride and, subsequently, carbonized at temperatures up to 1400 °C to yield the appropriately modified carbon materials with improved oxidation resistance characteristics [2b]. In yet another related study, a petroleum pitch has been modified with colloidal silica followed by carbonization at elevated temperatures yielding under argon a mixture of α- and β-SiC at around 1600 °C [2c]. Finally, co-pyrolysis of triphenylsilane with aromatic residues from petroleum oil distillation has been investigated providing interesting clues about some important interactions of mesophase spheres with the silicon precursor at 440 °C [2d].

Our earlier studies were concerned with co-pyrolysis of a pitch binder with the selected silicon precursors, i.e. Si, SiO₂, SiC, poly(carbomethylsilane) $\{-CH_2-Si(CH_3)H-\}_n$ [3,4]. In all systems, at temperatures up to 1650 °C the formation of β-SiC homogeneously distributed in the evolving carbon matrix was confirmed. The beginning of SiC formation was observed after the 1300 °C pyrolysis stage in the Si/pitch and poly(carbomethylsilane)/pitch systems while for SiO₂/pitch higher than that temperatures

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were required. Even in the case of the commercial SiC/pitch system some changes were detected that were, likely, due to carbothermal reduction within SiO₂ passivation layers and formation of a secondary surface β-SiC phase.

In this regard, siloxane polymers (polysiloxanes) deserve a deal of attention as the pool of inexpensive silicon precursors for pitch modifications. It was shown that weight losses during pyrolysis of pure polysiloxanes at 1400 °C ranged from 20 to 30% [5]. At 400–800 °C, the evolution of relevant hydrocarbons took place and at 600–1000 °C dihydrogen was given off. It was concluded that the initial polymer was converted in the 600–800 °C range to an amorphous inorganic network of hydrogenated oxycarbide tetrahedral units SiC_aO_b, $a + b = 4$, and that above 800 °C some excess carbon started to crystallize in turbostratic forms. From 1100 to 1600 °C, crystallization of SiC and minor SiO₂ took place.

In another work, simple polysiloxanes were studied as potential binders for sintering polycrystalline SiC bodies [6]. The pyrolysis of the precursors at 1200–1500 °C yielded an amorphous Si–O–C phase. After heating at 1600 °C, the product consisted of β-SiC and residual SiO₂ with the excess of C in the form of glassy carbon domains of 3.5 nm in size.

In regard to the polysiloxane/pitch system, thermal decomposition of the polysiloxanes in the reactive environment of simultaneously carbonized pitch may offer advantageous reaction pathways with enhanced cross-linking chemistry occurring at lower temperatures. Herein, we employ poly(dimethylsiloxane) admixed with a binder pitch to study the formation of SiC during co-pyrolysis up to 1650 °C and compare it with the related system SiO₂/pitch.

2. Experimental

2.1. Substrates

A typical coal tar pitch utilized as a binder in graphite electrode industry was used (C, 93.5%; Mettler's s.p., 101.5 °C; toluene insolubles TI, 20.9%). An air-cured solid dimethylsiloxane polymer, PDMS, was applied as a target silicon precursor ('Organika-Sarzyna', Poland); for initial liquid PDMS: av. composition {–O–Si(CH₃)₂–}_n; viscosity (25 °C), 10⁴ cSt; MW, approx. 60,000 amu; density, 0.97 g/cm³. Due to a limited solubility of PDMS in a molten pitch, the precursor was first cured in air at 300 °C for 24 h resulting upon oxidation-assisted cross-linking in a soft solid: Si (obtained), 37.9% vs. Si (calculated in {–O–Si(CH₃)₂–}_n), 37.9%. The solid was ground below 0.02 mm and applied at 20 wt% with the pitch. In addition, silica SiO₂ (Aldrich), <325 mesh, was used after preliminary calcination at 900 °C, 1 h, to remove adsorbed water; the silica was applied at 27.4 wt%.

2.2. Procedures

The powder substrates were first homogenized as solids, followed by a 30-minute stirring in the molten pitch at 160 °C. Upon cooling to RT and grinding, the stirring was repeated at 160 °C followed by cooling to RT and final grinding. Each mixture, including a reference pure pitch (not modified), was subsequently pyrolyzed at 500 °C, for 1 h, under an argon atmosphere to afford the initial carbonizates. After grinding, each of them was split into two parts with one part subject to pyrolysis under argon at 1300 °C and the other at 1650 °C with a 1 h hold time. In a few cases, a chunk of a solid carbonizate from the pyrolysis at 500 °C was preserved as-is (not ground) and pyrolyzed with the original bulk powder to afford specimens for additional SEM examinations.

2.3. Characterization

For Si-contents, 'wet' chemical analysis was utilized to ashes from samples combustion at 815 °C. There were two major sources of inaccuracies in Si-determinations. First, white deposits on the edges of crucible were observed that suggested losses of silicon species upon ashing and, second, some HF-insoluble black residues were occasionally observed in the systems with the precursors. XRD diffractograms were collected on a Bruker D8 Advance diffractometer using a Co-source. Identification of crystalline phases was accomplished with the help of Bruker database as well as literature data [7]. FT-IR spectra were acquired for KBr pellets with a Biorad Analytical Digilab in the 400–4000 cm^{–1} range. XPS data were determined with a Vacuum System Workshop Ltd instrument equipped with a Al K_α X-ray radiation source (1486.6 eV, 200 W) and spectral energies were referenced vs. that of carbon (284.6 eV). SEM micrographs were taken both for the larger chunks of carbonizates and their powders with JEOL 5400 scanning electron microscope.

3. Results and discussion

Fig. 1 shows the yields of the carbonizates in function of pyrolysis temperature. It is apparent that for the initial carbonization step at 500 °C the composite systems show similar yields, i.e., for PDMS/pitch and SiO₂/pitch, 67% and 70%, respectively, and the yield for pure pitch is lower at approx. 60%. These numbers reflect, after all, the fact that the silicon precursors are quite weight stable under such conditions and the observed weight losses are attributed mostly to pitch carbonization. This is especially true with regard to non-volatile SiO₂ that is expected to interact with pitch constituents, if at all, only in surface type reactions with insignificant weight-related effects. On the other hand, for the cured PDMS one can expect at 400 °C some intrinsic structure decomposition [8]. This has

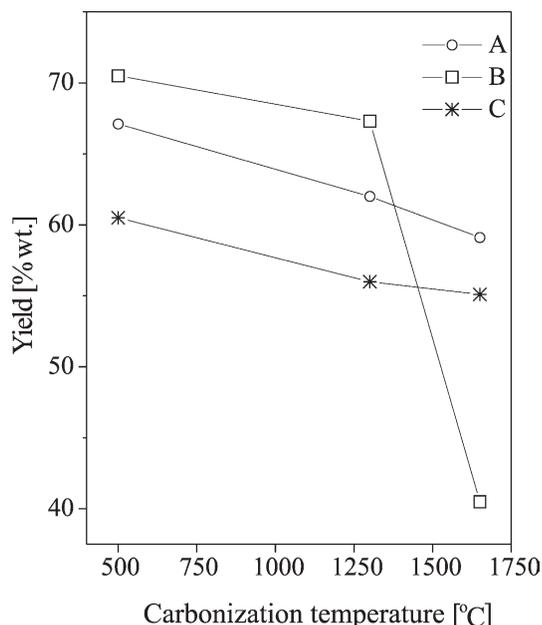


Fig. 1. Yield of carbonizates with temperature for: (A) poly(dimethylsiloxane)/pitch, (B) SiO₂/pitch, (C) not modified pitch; connecting lines are guides for eye.

to be confronted with our Si-analyses of the ashed residues that show 4.9 wt% of Si after the 500 °C treatment to be compared with the initial Si content of 7.6 wt% before pyrolysis. Apparently, some silicon losses occurred under applied conditions, likely, due to the evolution of plausible low molecular cyclosiloxanes known to form during the decomposition of polysiloxanes [9].

After carbonization at 1300 °C, rather small weight losses are continued for both composite carbonizates. They parallel the changes for the non-modified carbonizate indicating similar weight loss characteristics, most likely, associated with the evolution of volatiles from the carbonaceous matter. Further carbonization at 1650 °C results in the dramatic weight loss in the SiO₂/pitch system. For not modified carbonizate, one observes slowing in volatiles evolution while for the system PDMS/pitch the trend resembles more of the system SiO₂/pitch; note

the curve flattening effect in the PDMS/pitch system due to the smaller precursor's content. Regarding the SiO₂/pitch system, the observed weight changes after the treatment at 1650 °C can be linked to the carbothermal reduction of silica in this temperature range according to the general equation: $\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$. The formation of SiC is accompanied by the evolution of significant CO gas at the expense of C and O from the system. Similar reactions are expected to operate in the PDMS/pitch system and, therefore, the overall character of weight changes should also be similar in that case (bending down of the curves in the 1300–1650 °C range). However, the formation of the transient SiO_xC_y species in the PDMS/pitch system, wherein carbon is also derived from the polymer functionalities and not only from the carbonized pitch matrix, may relatively decrease the total weight loss compared with the silica case [5,10,11].

The SEM images displaying the typical morphology of the 1300 °C carbonizates are included in Fig. 2. Fig. 2a for the carbonizate from the PDMS/pitch system shows a compact body with no apparent microporosity. In Fig. 2b for the material from the SiO₂/pitch system, the lighter particle-like features scattered throughout the solid nonporous body may well correspond to unreacted SiO₂ grains quite homogeneously distributed within the observed carbonizate's particle. It is worth mentioning that in the latter material occasional SiC whiskers are observed on particles surfaces while no such materials forms are detected in the PDMS/pitch material from this temperature [12].

The FT-IR spectra for the systems are shown in Fig. 3 including the spectrum for the conditioned solid PDMS which is basically the same as a spectrum for the parent liquid PDMS (not shown); the anticipated small progression of curing-promoted cross-linking with a degree of Si–O bond network expansion at the expense of some ≡Si–CH₃ groups does not visibly influence the relevant spectra. The bands at about 1100 cm⁻¹ and 810 cm⁻¹ are typical of the Si–O bond modes and those at about 840 cm⁻¹ and 1260 cm⁻¹ of the Si–C bonds (in ≡Si–CH₃) while the strong bands at 2900–2970 cm⁻¹ are for the C–H

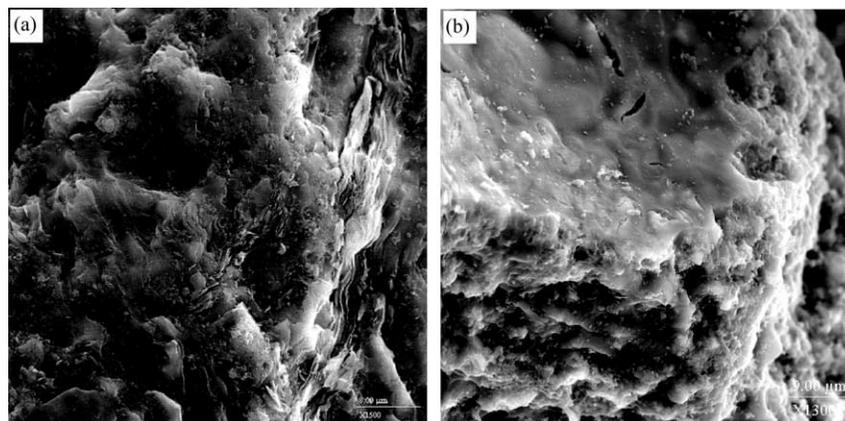


Fig. 2. SEM images of powder products after carbonization at 1300 °C, 1 h, Ar atmosphere: (a) poly(dimethylsiloxane)/pitch; (b) SiO₂/pitch.

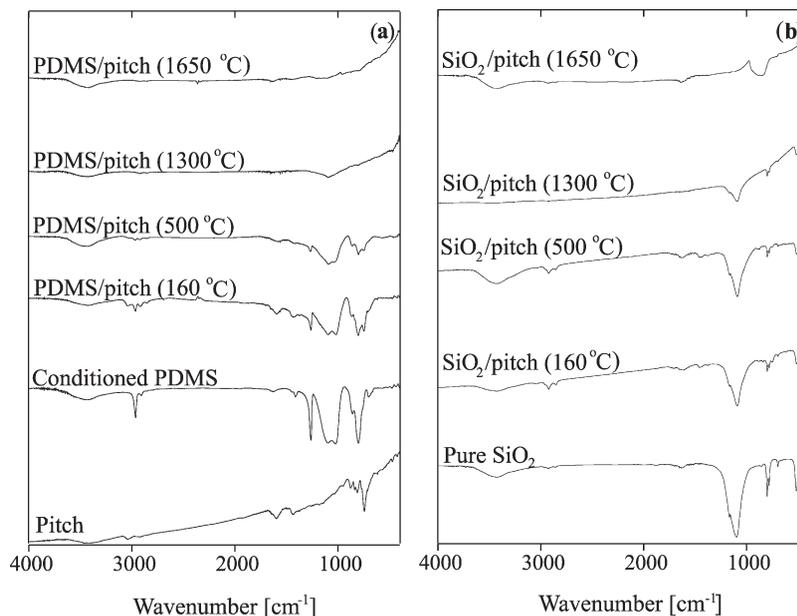


Fig. 3. FT-IR spectra for materials from the systems: (a) PDMS/pitch; (b) SiO₂/pitch.

vibrations [13]. The IR spectra for the 160 °C-homogenized mixtures are best described as the composite spectra of the two components contributions. The first noticeable changes are observed in the spectra for the carbonizates obtained at 500 °C. Significantly decreased are the intensities of the bands associated with C–H functionalities (mostly, –CH₃ groups) which indicates both the progressive carbonization of the pitch and, in particular, for the PDMS/pitch system, polymer decomposition/condensation chemistry resulting in a decreased number of the ≡Si–CH₃ groups [8]. It is worth pointing out that under such circumstances, there is likelihood of interactions of the two decomposing matrices, i.e., carbonaceous one from the pitch and the silicate one from PDMS, as well as process by-products. The further carbonization at 1300 °C results in the spectrum displaying the strong band at about 1100 cm⁻¹ for the Si–O stretches as well as an enhanced band at about 840 cm⁻¹ assigned to the Si–C stretches. This is accompanied by the significantly diminished bands in the 2900–2970 cm⁻¹ range characteristic of C–H bonds. The spectra for the 1650 °C carbonizates contain mostly the Si–C band at 840 cm⁻¹ and still persisting weak Si–O band at 1100 cm⁻¹; the latter may, however, be more an effect of a secondary SiO₂ passivating surface layer formed during sample handling than assigned to unreacted polymer-based Si–O moieties. In this regard, the broad band at about 3400–3600 cm⁻¹ is typical of O–H stretches in adsorbed water.

The comparison of the IR spectra for both precursor systems entitles to the conclusion that similar chemical changes take place during their carbonization. The spectra suggest that, despite different chemical environments, the Si–O bonds in the two precursors are quite stable and only the treatment at 1650 °C results in their carbothermal reduction and formation of SiC.

Fig. 4 represents the XRD patterns obtained in the PDMS/pitch (a) and SiO₂/pitch (b) systems. Note that the initial solid PDMS is amorphous. Therein, the first significant structure ordering effects are seen after the 1300 °C treatment and concerning with graphite-like domains in the evolving C-matrix (broad halo at approx. 2θ = 30° for the (00.2) plane). On the other hand, crystallization of nano-SiC is detected after the carbonization at 1650 °C (e.g., the strongest (111) peak at 2θ = 42° for β-SiC) which is accompanied by increased C-ordering processes. It also appears that the silicon precursor's conversion to SiC does not significantly influence the simultaneous evolution of graphitic domains. In this regard, our earlier studies of the Si/pitch and polycarbosilane/pitch systems indicated an inhibitive effect of those precursors on the concurrent to SiC formation–graphitization processes [3,4].

As seen from Fig. 4b, the diffractions due to the presence of crystalline SiO₂ persist up to the 1300 °C stage while the evolution of the ‘graphitic’ diffraction at about 2θ = 30° seems to be somewhat hampered compared to the previously discussed case of the PDMS/pitch system. Such an impact of the SiO₂ component may reflect both its relatively higher concentration (mostly as a result of Si-losses in the PDMS/pitch system) and more extensive C-consumption in carbothermal reactions during the 1650 °C carbonization. Finally, for both systems, the carbonization at 1650 °C results in the efficient conversion of the precursors to the major regular β-SiC with some detectable hexagonal α-SiC polytypes. The average crystallite diameters are determined from the Scherrer's equation for the β-SiC phase (k = 1) yielding 60 nm and 71 nm in the PDMS/pitch and SiO₂/pitch 1650 °C carbonizates, respectively. The similar nanosized region of SiC formation in both systems is evident.

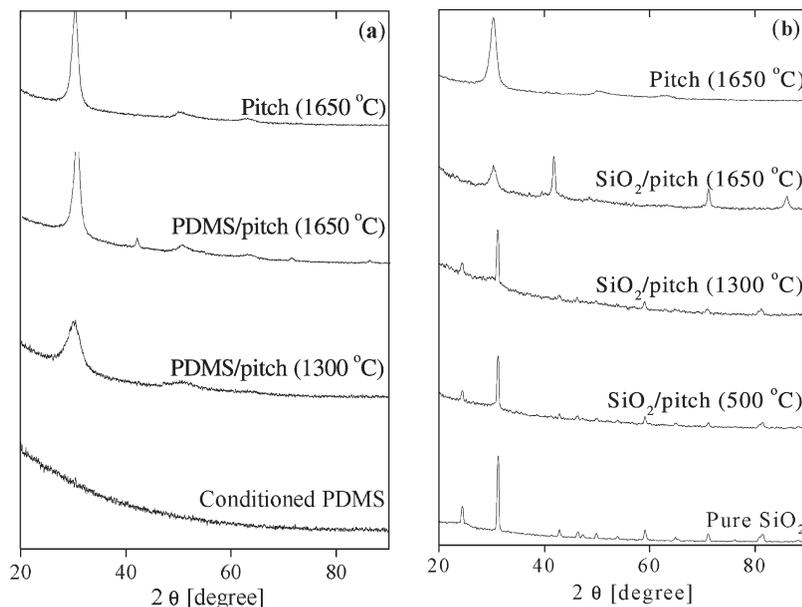


Fig. 4. XRD patterns for materials from the systems: (a) PDMS/pitch; (b) SiO₂/pitch.

The XPS spectra of the Si 2p and C 1s bands for materials from the poly(dimethylsiloxane)/pitch system are shown in Fig. 5a and b, respectively, with the horizontal lines referring to typical literature data ranges for the specified bonds. The Si 2p peak at about 102 eV is characteristic of the Si–O bonds in the polymer as corroborated by the FT-IR results above. This peak also lies in the region of SiO_xC_y species. After the 500 °C carbonization, this peak is shifted toward higher energies. Band deconvolution (not shown) yields two peaks, one at about 103 eV for the Si–O bonds and another at 105 eV for the likely surface Si–O moieties. For the 1300 °C composite, the Si 2p band becomes narrower and shifts to lower energies still within the range

of the silicon in oxygen-rich environments; note, the lack of significant reduction chemistry is also supported by the IR and XRD data. The final carbonization at 1650 °C results in shifting the Si 2p band even more toward lower energies with the major peak at 101 eV typical for SiC; however, a broadening of the peak indicates some contribution from the SiO_xC_y species. One has to be aware of the fact that XPS is a surface sensitive technique delivering information about average bonding environments within a surface layer typically 1–7 nm deep. Therefore, the pronounced tendency of Si-bearing composites to acquire SiO₂ passivation layers upon exposure to humid air may, partly, be responsible for the detection by XPS and FT-IR of the Si–O functionalities

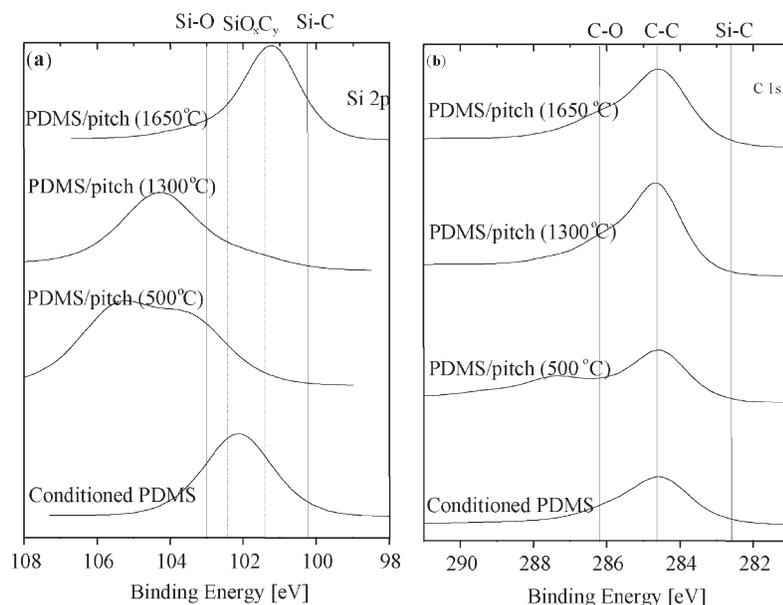


Fig. 5. XPS spectra for materials from the system PDMS/pitch: (a) Si 2p line; (b) C 1s line.

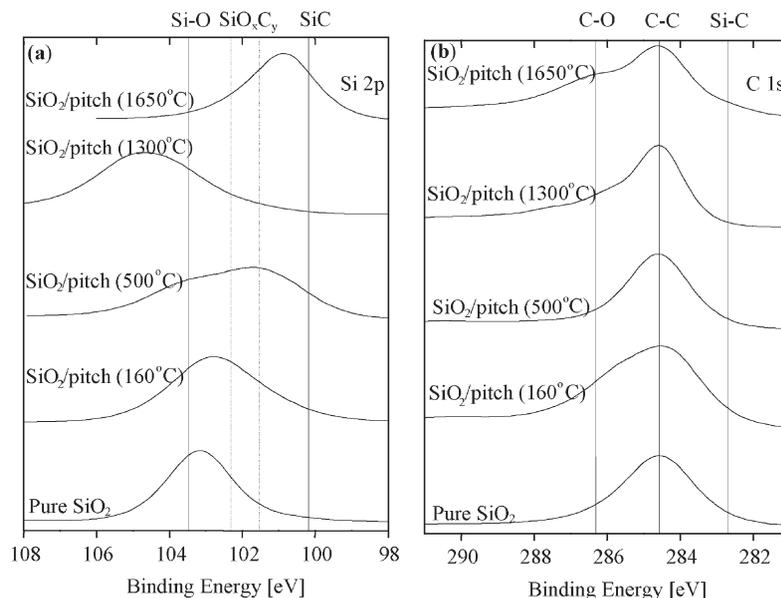


Fig. 6. XPS spectra for materials from the system $\text{SiO}_2/\text{pitch}$: (a) Si 2p line; (b) C 1s line.

even after the carbothermal reduction chemistry significantly progressed or was completed. Finally, the appearance of the relevant C 1s lines supports the qualitative conclusions above.

Fig. 6 displays the XPS data for the $\text{SiO}_2/\text{pitch}$ system. The changes of the Si 2p band with carbonization temperature are shown in Fig. 6a. Generally, the changes are qualitatively similar to those observed in the PDMS/pitch system. Specifically, some line broadening and high energy shifting of the bands after the 500 °C stage likely result from chemical reactions between the surface functionalities on SiO_2 particles and reactive pitch constituents with the formation of transient surface SiO_xC_y species. The deconvolution of the Si 2p band in this case yields a major peak at about 103.5 eV characteristic of the SiO_2 bonding environments and, therefore, supports the presence of mostly unreacted silica. Similarly as in the case of the PDMS/pitch system, shifting of the peak toward higher energies is detected for the 1300 °C carbonizate. Only after the 1650 °C carbonization stage, the Si 2p peak is found in the typical for SiC region at about 101 eV. A broadening of the peak supports the presence of surface SiO_xC_y species likely resulting from the sample's exposure to humid air.

4. Conclusions

We successfully prepared homogeneously dispersed mixtures of a coal tar pitch with (i) air-cured solid poly(dimethylsiloxane), PDMS, and (ii) silica powder, SiO_2 , for a stepwise carbonization of the two binary precursor systems up to 1650 °C. There were indications of some Si-losses from the PDMS/pitch system after the carbonization at 500 °C most likely due to the evolution of

volatile cyclosiloxane polymer decomposition by-products under applied conditions. The prevailing conversion of the silicon precursors to silicon carbide was detected in both cases only after the final carbonization stage at 1650 °C. The nano-SiC/C composites obtained at this temperature were characteristic of the comparable nanosized regime of SiC particles, i.e., 60–70 nm, that indicated basically similar conversion/crystallization processes in both systems. These processes could be linked to the major chemical event in the systems, namely, the carbothermal reduction of the Si–O moieties leading to SiC. However, some specific reaction pathways were observed in the $\text{SiO}_2/\text{pitch}$ system resulting in occasional SiC whisker formation. On the other hand, the presence of intrinsic carbon in PDMS and its ability to efficiently transform to transient SiO_xC_y species upon polymer decomposition at relatively low temperatures positively inflicted upon the overall conversion characteristics in the PDMS/pitch system.

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