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XRD and ^{29}Si MAS NMR spectroscopic studies of carbon materials obtained from pyrolyses of a coal tar pitch modified with various silicon-bearing additives

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Abstract

A typical coal tar pitch used in manufacturing of graphite electrodes was individually modified with various silicon-bearing additives yielding mixtures that were pyrolyzed (carbonized) stepwise at increased temperatures up to 1650 °C. Three commercially available additives such as the elemental Si, silica SiO₂, and poly(carbosilane) $\{-\text{CH}_2-\text{SiH}(\text{CH}_3)-\}_n$ as well as reference silicon carbide SiC were used. The resulting intermediate and final materials were studied with the XRD and ^{29}Si MAS NMR methods. For two additives, i.e., elemental Si and poly(carbosilane), the beginning of their conversion to SiC was detected at 1300 °C while for SiO₂ higher temperatures were required under applied conditions.

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1. Introduction

The many advantageous properties of silicon carbide SiC have made it a valuable component of carbon-based composites including carbon/graphite materials widely

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utilized in metallurgy. Especially attractive are its thermal shock resistance and stability, and compelling mechanical strength all coupled with remarkable chemical inertness under demanding industrial applications [1]. Regarding the synthetic routes to SiC in carbon materials, there have been extensive studies on chemical vapor deposition techniques (CVD) including the related infiltration deposition method, which enable the formation of thin SiC layers on the material's surface [2]. Another approach relies on the chemically engineered formation of finely dispersed SiC particles in the bulk of the carbon material's matrix.

Coal tar and petroleum pitches, due to their inherent chemical properties, mesophase formation, and low melting points, appear to be promising candidates for modifications with silicon-bearing additives serving both as the source of reactive C-atoms toward SiC and the C–C matrix. For example, a mixture of electrographite, anthracite, and a pitch binder has been admixed with elemental silicon, and processed under industrial conditions of carbon electrode manufacturing [3]. In another work, a petroleum pitch has been modified with organo-derivatives of silicon and aluminum and, subsequently, carbonized at elevated temperatures to yield modified carbon materials with improved oxidation resistance characteristics [4]. In yet another related study, a petroleum pitch has been modified with colloidal silica followed by carbonization at elevated temperatures yielding a mixture of α - and β -SiC at around 1600 °C [5].

The subject of the current study is the modification of a typical coal tar pitch used in graphite electrode industry with selected Si-bearing additives followed by the carbonization process at increased temperatures, while temperature-dependent transformations of the additives to SiC are monitored mainly with the XRD and ^{29}Si MAS NMR spectroscopic methods.

2. Experimental

A typical coal tar pitch binder was utilized as the source of carbon (C, 93.5%; softening by Mettler, 101.5 °C; TI, 20.9%). The following silicon-bearing additives purchased from Aldrich were used: elemental Si <325 mesh (A), silica SiO₂ <325 mesh (B), poly (carbosilane), $\{-\text{CH}_2-\text{SiH}(\text{CH}_3)-\}_n$, m.p. 79 °C (D), and for reference samples, commercial SiC <400 mesh (C). 15 wt.% contents of the additives were applied as calculated per elemental Si in sample. For homogenization, the mixtures were heated to 160 °C to ensure a liquid medium of the molten pitch and stirred for 30 min. This was followed by carbonization at 500 °C, 1 h, Ar atmosphere. After characterization, the remaining material was carbonized at a higher temperature, i.e., first at 1300 °C and finally, at 1650 °C yielding black carbonizates. XRD spectra were collected with the Bruker D8 Advance Diffractometer using Co radiation source. Crystalline phases were identified with an available database and using literature data [6]. ^{29}Si MAS NMR spectra were collected on a homemade pulse NMR spectrometer at 59.517 MHz (magnetic field 7.05 T). A Bruker HP-WB high-speed MAS probe was used to record spectra at 4 kHz spinning speed. The FID was recorded after a single 3 μs rf pulse or $\pi/2$ flipping angle. The acquisition delay used in accumulation was 600 s, and the number of acquisitions ranged from 32 to 220, depending on signal strength. The ppm scale was referenced to the

^{29}Si resonance of TMS. All NMR spectra were normalized to the same number of acquisitions and to the same mass of the sample. Additionally, the spectral intensities for the pure additives were scaled to 0.15 to normalize them with the modified carbonizates.

3. Results and discussion

Fig. 1 presents the yields of the carbonizates individually modified with 15 wt.% of the selected Si-bearing additive including a carbonizate from nonmodified pitch. The comparable yields of the modified carbonizates are obtained after carbonization at 500 °C, i.e., approx. 70%. This temperature level causes very extensive, complex decomposition and condensation reactions in the carbonaceous material that constitutes the initial pitch [8]. In such a reactive environment, one could expect chemical reactions involving at least one of the additives. Namely, the poly(carbosilane), $\{-\text{CH}_2-\text{SiH}(\text{CH}_3)-\}_n$, with the reactive hydride functionality should preferentially react and chemically bind to the progressively condensing network of the C-atom matrix and/or undergo self-condensation reactions. Under these conditions, other additives like elemental Si, SiO_2 , and SiC could, at the most, be involved in the surface type of reactions with pitch components with the participation of their surface $-\text{OH}$ groups.

In the subsequent heating stage at 1300 °C, a steady weight loss is observed for all the carbonizates. While it is relatively small and comparable for the Si, SiO_2 , and SiC additives, where it likely corresponds to a progressing elimination of volatiles from the semi-coke, it is rather large for the poly(carbosilane). In the latter case, the intrinsic decomposition of this compound towards SiC according to: $\{-\text{CH}_2-\text{SiH}(\text{CH}_3)-\}_n \rightarrow n\text{SiC} + \{\text{C}_n\text{H}_{6n}\}$, where $\{\text{C}_n\text{H}_{6n}\}$ designates in short the likely volatile by-products (hydrocarbons, hydrogen), is expected to be the major weight loss factor [9].

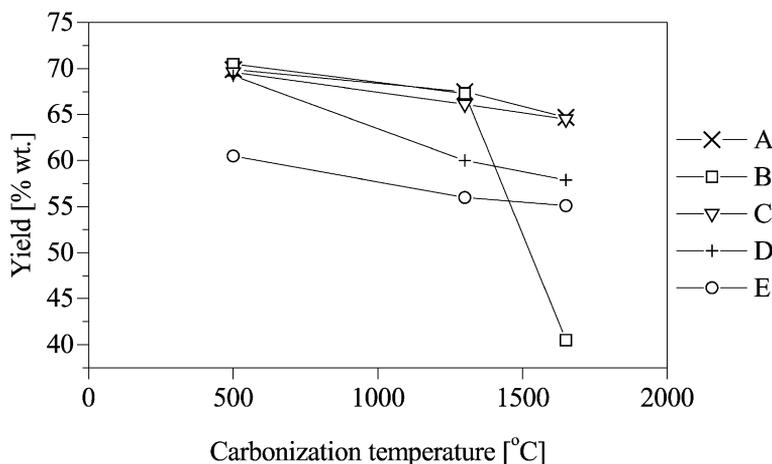


Fig. 1. Overall yields of the carbonizates obtained from coal tar pitch modified with: (A) elemental Si; (B) SiO_2 ; (C) SiC; (D) poly(carbosilane); (E) carbonizate from nonmodified pitch.

A pronounced weight loss occurs for the SiO₂-containing material after carbonization at 1650 °C and, apparently, the carbothermal reduction of SiO₂ according to an idealized equation: $\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$, is responsible for it. In this case, the removal of oxygen from SiO₂ and carbon from the carbonaceous phase in the form of volatile CO is the major contributing factor. It is worth mentioning that the carbothermal reduction of silica can, in fact, be more complex than shown above [10a].

Fig. 2 includes the XRD patterns for the modified pitch materials at different stages of their conversion including the pattern for the commercial SiC at RT, which happens to be a mixture of the 4H and 6H SiC polytypes. There is a detectable formation of SiC after carbonization at 1300 °C for the elemental Si and poly(carbosilane) additives and the significant line broadening suggests nanocrystalline SiC in these cases. There is no clear XRD evidence for any significant SiC to be formed with the SiO₂ additive after the 1300 °C carbonization step, indicating that its carbothermal reduction is efficient at still higher temperatures under applied conditions. This is in good agreement with the literature reports for the related SiO₂-containing systems [10]. In all cases, the formation of the major β-SiC phase is evident after the 1650 °C treatment, while for the samples that already contained SiC after the 1300 °C carbonization, now, the XRD peaks are more intense and sharper, indicative of an increased crystallinity.

There is also an additional effect of the additives conversion to SiC, namely, a modification of the degree of C-atom ordering in the graphitic-like structures constituting

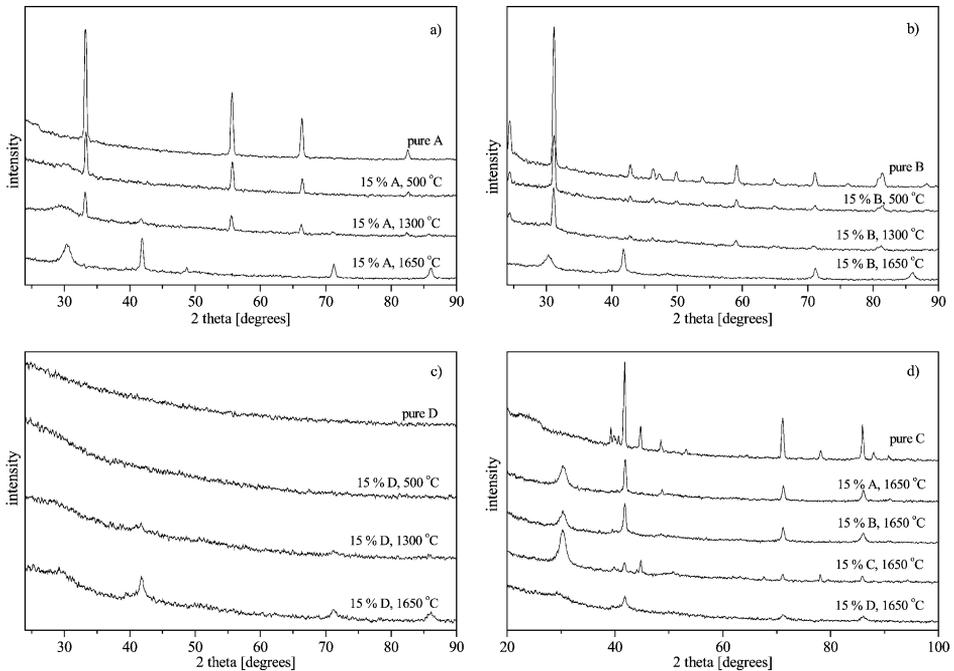


Fig. 2. XRD patterns for carbonizates modified with: (a) Si (A); (b) SiO₂ (B); (c) poly(carbosilane) (D); insert d) contains the patterns for all 1650 °C materials including the pattern for pure SiC (C).

the carbon matrix. For instance, in the case of the elemental Si (A) and carbonization at 1300 °C, there is a broad line at approx. $2\theta = 30^\circ$ characteristic of diffractions at the graphitic-like layers of C-atoms. After the 1650 °C carbonization, this line increases in intensity and sharpens due to an improved long-range ordering within such the C-structures. On the other hand, for silica (B), a detectable broad peak in this region appears only after the 1650 °C carbonization, while for poly(carbosilane) (D), the peak appears both after the 1300 and 1650 °C treatments; the prevailing broad line is quite weak. These observations may suggest an inhibitive effect of the early formed nanosized SiC particles on the parallel C-ordering process.

Utilizing Scherrer's equation ($K=1.0$), average crystallite sizes of SiC are calculated indicating the nanosized regime of the crystallites (Table 1). Based on these data, in all cases the regular 3C phase of SiC is prevailing formed; additionally, the minor hexagonal 6H polytype is detected in the carbonizates made with the SiO₂ and poly(carbosilane) additives, which can partly be understood by the specific phase changes for SiC taking place under applied conditions [11].

The collected ²⁹Si MAS NMR spectra are shown in Fig. 3. It should be stressed that in contrast to the XRD technique, which is sensitive to crystalline phases only, the NMR spectrum reflects all silicon atoms in the sample independently on their long-range order, thus, providing supplementary structure information to the XRD study. In this regard, the single peak at –80.6 ppm for elemental Si (A) and the peak at –107.3 ppm for silica (B) fall well within the range known for these species [7] as well as two broad and overlapping peaks at 0 and –18 ppm for poly(carbosilane) (D) [12]. The three peaks of roughly equal intensities at –14.8, –20.8, and –25.2 ppm seem to represent the 6H polytype of SiC (C) [13].

It can clearly be seen for the samples carbonized at 500 °C that the crystalline nature and quantities of the elemental Si, SiO₂, and SiC additives are preserved after the treatment; the peaks are in the same positions and their widths are comparable (FWHM approx. 120 Hz or less). In the case of poly(carbosilane), a significant reduction of the –18 ppm peak's intensity representing the SiC₃H units as compared to the 0 ppm peak due to the SiC₄ units [13] may be caused by the reactions of the Si-hydrogen atoms between the individual poly(carbosilane) chains and/or with the carbonaceous matrix. A similar effect on the ²⁹Si NMR shifts has been reported for pure poly(carbosilane) pyrolyzed at 500 °C [13].

Table 1
XRD-derived crystallite sizes of the SiC polytypes in carbonizates

Sample (additive)	SiC polytype	Crystallite size, L_c (nm)	
		1300 °C	1650 °C
A (elemental Si)	3C; major (β -SiC)	58	101
B (SiO ₂)	3C; major (β -SiC)	–	71
	6H; minor (α -SiC)	–	11
C (SiC)	6H; major (α -SiC)	–	76
	4H; minor (α -SiC)	–	390
D (poly(carbosilane))	3C; major (β -SiC)	Not determined	28
	6H; minor (α -SiC)	–	8

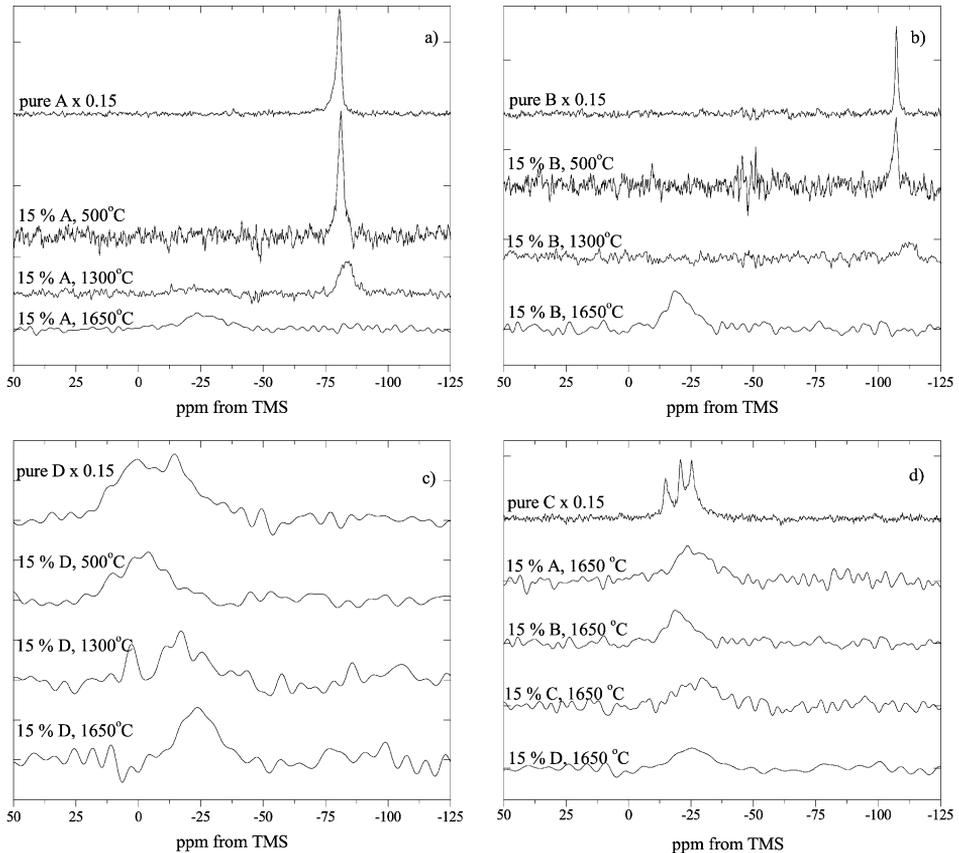


Fig. 3. ^{29}Si MAS NMR spectra for carbonizates modified with: (a) Si (A); (b) SiO_2 (B); (c) poly(carbosilane) (D); insert d) contains the spectra for all 1650 °C materials including the spectrum for pure SiC (C).

A large change can be observed in the spectra after carbonization at 1300 °C; the lines become very broad (FWHH approx. 420 Hz) while their positions remain close to those observed in the initial microcrystalline compounds. It means that although the long-range order is markedly destroyed, the local atom arrangement still corresponds to the original additive's chemical make-up. Regarding material B, an analogous behavior was seen for SiO_2 after pyrolysis at 800 °C in the precursor system prepared from TMOS and phenol resin [14]. Although for sample A the related XRD pattern shows the nanocrystalline 3C SiC polytype, a barely visible bump on the baseline at -25 ppm can only be observed in the corresponding ^{29}Si MAS NMR spectrum suggesting, at first glance, an amorphous phase. We think, however, that an alternative explanation would rather emphasize the nanocrystalline nature of this phase.

Profound changes occur in the materials carbonized at 1650 °C. The lines are very broad (FWHH approx. 900 Hz) and they are centered at about -25 ppm for samples A and C, and at about -19 ppm for sample B, corresponding to the hexagonal and cubic

SiC, respectively [12]. Also, in our 1650 °C carbonizates A and B, no signals can be detected for the unreacted initial silicon-bearing compounds.

Due to the poor S/N ratio, it is difficult to unequivocally tell if the broad lines for the new SiC phase(s) represent a single SiC amorphous phase rather than resulting from a superposition of various nanocrystalline SiC polytypes, which would all have the peaks in the same ppm range. Although more than 200 polytypes of SiC have been reported, the number of nonequivalent Si-sites is a maximum of four, each of them characterized by a unique but slightly different chemical shift in the ^{29}Si NMR spectrum [12]. We are aware of only one successful analysis of the ^{29}Si NMR line as the superposition of two lines arising from the cubic and hexagonal phases of SiC [15]. This was done for the microtwinning crystals in the 1–2 μm size range; hence, they were at least an order of magnitude larger than in the present study.

In regard to the above, the ^{29}Si NMR spectra of the so-called amorphous SiC display a single, broad line (FWHH approx. 1.1 kHz) in the range from –14.5 ppm for the ceramic fiber [7] to –15 ppm for the silicon and graphite intimate powder mixture prepared by high-energy milling [16], and to –16 ppm for the ceramics obtained from pyrolysis of the pure poly(carbosilane) at 1700 °C [13]. In the latter case, the material was believed to be mainly β -SiC with some traces of the α -SiC phase. Finally, a broad line at –18 ppm was reported in the rice hulls carbonized at 1450 °C and it was assigned to the β -SiC phase [17].

It is likely that the formation and crystallization processes of SiC—given the relatively short carbonization time of 1 hour—are in some cases limited only to a fraction of a given silicon-bearing additive. It would thus require longer carbonization times at 1650 °C in order to transform the whole as-formed SiC to a unique and stable microcrystalline phase. Only then would the ^{29}Si NMR, together with XRD, provide a definite answer regarding the structure(s) of the SiC component(s). Such experiments are planned in the near future as are studies on the impact of the SiC-precursor modified pitch binders on the practical properties of the resulting C-composites and prototype carbon/graphite materials.

In summary, the temperature and the type-of-additive dependence of the formation of SiC from the different Si-bearing additives in the complex chemical system with the coal tar pitch are demonstrated and discussed based on the results of the employed characterization methods.

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References

- [1] (a) Z.S. Rak, Key Eng. Mater. 206–213 (2002) 1049;
(b) D. Hourlier-Bahloul, Key Eng. Mater. 206–213 (2002) 15.
- [2] (a) E. Walasek, S. Jonas, T. Stapinski, S. Kluska, A. Czyzewska, Key Eng. Mater. 206–213 (2002) 567;

- (b) H. Sieber, E. Vogli, F. Muller, P. Greil, N. Popovska, H. Gerhard, *Key Eng. Mater.* 206–213 (2002) 2013;
(c) L.F. Pochet, P. Howard, S. Safaie, *Surf. Coat. Technol.* 86–87 (1996) 135;
(d) L.L. Snead, O.J. Schwarz, *J. Nucl. Mater.* 219 (1995) 3.
- [3] J. Szpineter, The influence of the Si-additive on the structure and properties of carbon materials. PhD Dissertation, Silesian Technical University, Katowice, Poland, 1999, in Polish.
- [4] P.P. Paul, S.T. Schwab, *Carbon* 34 (1996) 89.
- [5] L.A. Harris, C.R. Kennedy, G. Chia-Tsing Wei, F.P. Jeffers, *J. Am. Ceram. Soc.* C-121 (1984).
- [6] P.T.B. Shaffer, *Acta. Crystallogr. B* 25 (1969) 477.
- [7] J.S. Hartman, M.F. Richardson, B.L. Sherriff, B.G. Winsborrow, *J. Am. Chem. Soc.* 109 (1987) 6059.
- [8] D.W. Van Krevelen, *Coal*, Elsevier, Amsterdam, 1993.
- [9] (a) G. Chollon, M. Czerniak, R. Pailler, X. Bourrat, R. Naslain, J.P. Pillot, R. Cannet, *J. Mater. Sci.* 32 (1997) 893;
(b) E. Bouillon, F. Langlais, R. Pailler, R. Naslain, F. Cruege, P.V. Huong, J.C. Sarthou, A. Delpuech, C. Laffon, P. Lagarde, M. Monthieux, A. Oberlin, *J. Mater. Sci.* 26 (1991) 1333.
- [10] (a) R. Koc, S.V. Cattamanchi, *J. Mater. Sci.* 33 (1998) 2537;
(b) P.C. Silva, J.L. Figueiredo, *Mater. Chem. Phys.* 72 (2001) 326;
(c) S.-H. Chen, C.-I. Lin, *J. Mater. Sci. Lett.* 16 (1997) 702;
(d) C. Dai, X. Zhang, J. Zhang, Y. Yang, L. Cao, F. Xia, *J. Am. Ceram. Soc.* 80 (1997) 1274.
- [11] A.L. Ortiz, F.L. Cumbreira, F. Sanchez-Bajo, F. Guiberteau, H. Xu, N.P. Padture, *J. Am. Ceram. Soc.* 83 (2000) 2282.
- [12] D.C. Apperley, R.K. Harris, G.L. Marshall, D.P. Thompson, *J. Am. Ceram. Soc.* 74 (1991) 777.
- [13] G.D. Soraru, F. Babonneau, J.D. Mackenzie, *J. Mater. Sci.* 25 (1990) 3886.
- [14] H. Schneider, C. Jager, A. Mosset, H. Tanaka, M. Schmucker, *J. Eur. Ceram. Soc.* 15 (1995) 675.
- [15] S. Harrison, X. Xie, K.J. Jakubenas, H.L. Marcus, *J. Am. Ceram. Soc.* 82 (1999) 3221.
- [16] X. Xie, Z. Yang, R. Ren, L.L. Shaw, *Mater. Sci. Eng. A* 255 (1998) 39.
- [17] J.C.C. Freitas, F.G. Emmerich, T.J. Bonagamba, *Chem. Mater.* 12 (2000) 711.