Morphology and surface properties of carbonizates (C/SiC nanocomposites) obtained *via* pyrolysis of a coal tar pitch modified with selected silicon-bearing precursors

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Abstract—Morphology of carbon-based composite materials obtained from pyrolysis of a coal tar pitch admixed with selected silicon-bearing additives is discussed based on SEM/EDX observations, mercury porosimetry, BET surface area determinations, and helium density data. The silicon precursors used in the study included elemental silicon Si, silica SiO_2, poly(carbomethylsilane) $\{-CH_2-SiH(CH_3)-\}_n$, and commercial SiC. Each individual binary mixture, i.e. pitch/silicon additive, was first repeatedly homogenized at 160°C in the liquid medium of the molten pitch followed by carbonization at 500°C. In all cases, one part of the initial 500°C solid carbonizate was further pyrolyzed at 1300°C and another part at 1650°C under an argon flow resulting in nanocomposite products C/SiC. Differences in properties and morphology of the products were linked to specific chemical changes taking place in the reaction systems.

Keywords: Pitch; carbon materials; nanomaterials; silicon carbide; SiC; composites.

1. INTRODUCTION

Because of its robust chemical, thermal and mechanical properties, silicon carbide SiC has found numerous technological applications. For example, in electronics many of the compound's uses rely on its semiconducting properties while, simultaneously, exploiting advantageous thermal and chemical resistance at high temperatures [1, 2]. By the same token, SiC has been introduced as a modifier to a group of carbon/graphite materials where its significant resistance to oxidation and thermal shocks coupled with a low thermal expansion coefficient are utilized to improve the performance and lifetime of blast-furnace carbon/graphite linings in metallurgy [3, 4].

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Depending on the mode of SiC incorporation into a material's structure and on the type of applied silicon precursor, polycrystalline SiC with a range of crystallite sizes can be formed in the pores of carbon matrix [3], or a thin protective SiC layer can be produced on carbon grain surfaces [5]. It is worth pointing out also that nanosized SiC may improve properties of such C/SiC composite materials [6–8]. That is mostly why significant research efforts have recently been undertaken in the area of utilization of various silicon-bearing precursors as modifiers for carbon materials [9–19] that supplement the known method of using elemental silicon as a molten saturating agent for making SiC in porous carbons [11–13]; similarly, CVD methods of preparing SiC films have also shown to be promising in some cases [5, 15].

In order to achieve highly homogeneous distribution of SiC nanocrystallites in a modified carbon matrix, special and usually troublesome procedures already during initial preparation of precursors are required. In this regard, all methods for manufacturing carbon/graphite materials that employ mixtures of solid carbon precursors and low melting coal tar or petroleum pitch binders are especially well suited for efficient mixing/homogenization, since one can utilize potentially advantageous pre-modifications of the pitch with a silicon precursor in the liquid phase.

The authors of this study have recently reported the investigations of various pitch/ silicon precursors that provided an insight into thermally promoted conversion of the precursors in the matrix of simultaneously carbonized pitch toward nanocomposites C/SiC [20–22]. In the current report, major applicable properties of the C/SiC composites and, particularly, morphology and surface development are discussed.

2. EXPERIMENTAL

The target products included carbon materials prepared by thermal treatment (carbonization, pyrolysis) under an argon atmosphere at final temperatures of 1300°C or 1650°C of a typical coal tar pitch binder (softening point by Mettler, 101.5°C; toluene insolubles, 20.9%) that was individually pre-modified/mixed with selected silicon-bearing precursors. The following powdered silicon precursors were used (Aldrich): elemental Si (<325 mesh), silica SiO_2 (<325 mesh), commercial SiC (<400 mesh), and poly(carbomethylsilane) $\{-CH_2-SiH(CH_3)-\}_n$ (av. molecular weight, 800; m.p. 79°C). Comparable reference carbonizates were also prepared from a pure non-modified pitch. After repeated mixing/homogenization of the components at 160°C in the liquid medium of the molten pitch, the substrate mixtures were pyrolyzed at 500°C under an argon atmosphere to afford initial solid carbonizates for further pyrolysis at the final temperature of 1300°C or 1650°C. A detailed description of the preparation and materials spectroscopic characterization is provided elsewhere [20, 21, 23].

The composite C/SiC materials were characterized with (i) BET surface areas derived from standard low temperature nitrogen adsorption measured with Mi-

cromeritics Gemini 2360, (ii) helium density measurements with Micromeritics AccuPyc (fivefold helium purging), and (iii) mercury intrusion porosimetry carried out with Porosimeter 2000 by Carlo Erba Instruments (pressures from 1 atm to 2000 atm corresponding to approx. 15 000 nm to 7.5 nm pore diameter range, respectively); additionally, (iv) SEM images were acquired with JSM 5400 Jeol scanning electron microscope (20 kV accelerating voltage, samples coated with Au), equipped with microprobe Link Isis 300, for intentionally preserved chunks of the materials of approx. 10 mm in size.

3. RESULTS AND DISCUSSION

Table 1 includes the results of helium density and BET surface area determinations for all composites. The density data indicate basically similar values for samples A (pitch/Si), B (pitch/SiO$_2$), and C (pitch/commercial SiC) with the higher densities observed for the 1650°C carbonizates (2.37–2.43 g/cm^3) relative to the respective 1300°C carbonizates (2.15–2.28 g/cm^3). These values have to be compared with the literature density data for graphite, 2.26 g/cm^3, and SiC, 3.21 g/cm^3, and they all are higher than the densities measured for both carbonizates from the pure pitch, i.e. 2.04–2.09 g/cm^3 (sample E). The latter observation can be explained by virtue of the composites containing either (i) yet unreacted or partially reacted heavy silicon precursors in the presumed Si—O—C assemblages in relevant systems after pyrolysis at 1300°C or (ii) prevailing regular β-SiC formed upon the 1650°C treatment in all systems. The various structural forms of transient and final silicon species evolving in the pyrolyzed carbon matrix were previously described for these systems [20].

Compared with the above, the densities for sample D (pitch/poly(carbomethylsilane)), 1.76–1.83 g/cm^3, appear to be outstandingly lower even in relation to the respective values for the carbonizates from the pure pitch (sample E). Such low
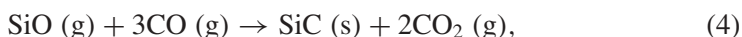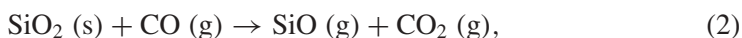
Table 1.

Helium densities, d_{He}, and BET surface areas, S_{BET}, of composites obtained from the systems: A pitch/elemental Si; B pitch/SiO$_2$; C pitch/commercial SiC; D pitch/poly(carbomethylsilane); E pure nonmodified pitch

| Sample	d_{He} (g/cm^3)		S_{BET} (m^2/g)	
	1300°C	1650°C	1300°C	1650°C
A	2.15	2.43	1.4	2.0
B	2.18	2.44	4.0	8.3
C	2.28	2.37	0.4	1.2
D	1.83	1.76	1.3	1.9
E	2.04	2.09	1.4	0.7

densities coupled with the established presence of nano-SiC in the composites [20] strongly imply the presence of abundant closed pores and make this material unique among the samples.

The low temperature nitrogen adsorption measurements indicate that all composites are characterized by rather small and, basically, comparable BET surface areas in the range 0.4–8.3 m^2/g. Among them, the composites from the pitch/SiO$_2$ system show the highest values of 4.0 m^2/g (1300°C) and 8.3 m^2/g (1650°C). Herein, the higher value detected in material after the 1650°C pyrolysis is thought to result mainly from the carbothermal reduction of silica to SiC taking place in this temperature range, and this is accompanied by consumption of carbon from the C-matrix and concurrent release of volatiles such as CO and/or CO$_2$ [24].

$$SiO_2 \text{ (s)} + C \text{ (s)} \rightarrow SiO \text{ (g)} + CO \text{ (g)}, \tag{1}$$

$$SiO_2 \text{ (s)} + CO \text{ (g)} \rightarrow SiO \text{ (g)} + CO_2 \text{ (g)}, \tag{2}$$

$$SiO \text{ (g)} + 2C \text{ (s)} \rightarrow SiC \text{ (s)} + CO \text{ (g)}, \tag{3}$$

$$SiO \text{ (g)} + 3CO \text{ (g)} \rightarrow SiC \text{ (s)} + 2CO_2 \text{ (g)}, \tag{4}$$

$$CO_2 \text{ (g)} + C \text{ (s)} \rightarrow 2CO \text{ (g)}. \tag{5}$$

Such surface-type reactions at temperatures required for the carbothermal reduction of silica can result in opening of closed pores and extension of existing ones thus producing materials with increased surface areas after the 1650°C treatment. However, some surface area increases are noticed also for other precursor systems even including the pitch/commercial SiC. In the latter case, our SEM study confirmed the existence of numerous cracks along C/SiC grains boundaries. These heterogeneities, on the one hand, could result from differences in thermal expansion coefficients of the two components of C/SiC. On the other hand, the microcracks could also evolve from secondary carbothermal reduction of the passivating SiO$_2$ layers as supported by FT-IR spectroscopic studies of the system [23]. Eventually, in all cases where carbon in the matrix is consumed in reactions with the precursors, one could envision increased surface areas of the composites mostly in the form of meso- and macropore contributions. Figure 1 shows low magnification images of two composites obtained at different pyrolysis temperatures from the same pitch/SiO$_2$ system that support the discussed morphological/surface area changes, at least, on the surfaces of the material grains.

Figure 2 represents typical results on porosity for the materials of interest collected from mercury porosimetry including the carbonizates made from the pure non-modified pitch. Figure 2A shows the cumulative pore volumes as a function of pore diameters for the 1300°C carbonizates while Fig. 2B shows similar results after the 1650°C pyrolysis. It is apparent from Fig. 2A that the visibly highest porosity is evident for the 1300°C non-modified carbonizate and that a similar alas lower porosity is observed for the carbonizate from the pitch/elemental Si system. At this stage of precursors conversion, i.e. after 1300°C treatment, one can expect either unreacted (pitch/SiO$_2$) or partially reacted (pitch/elemental
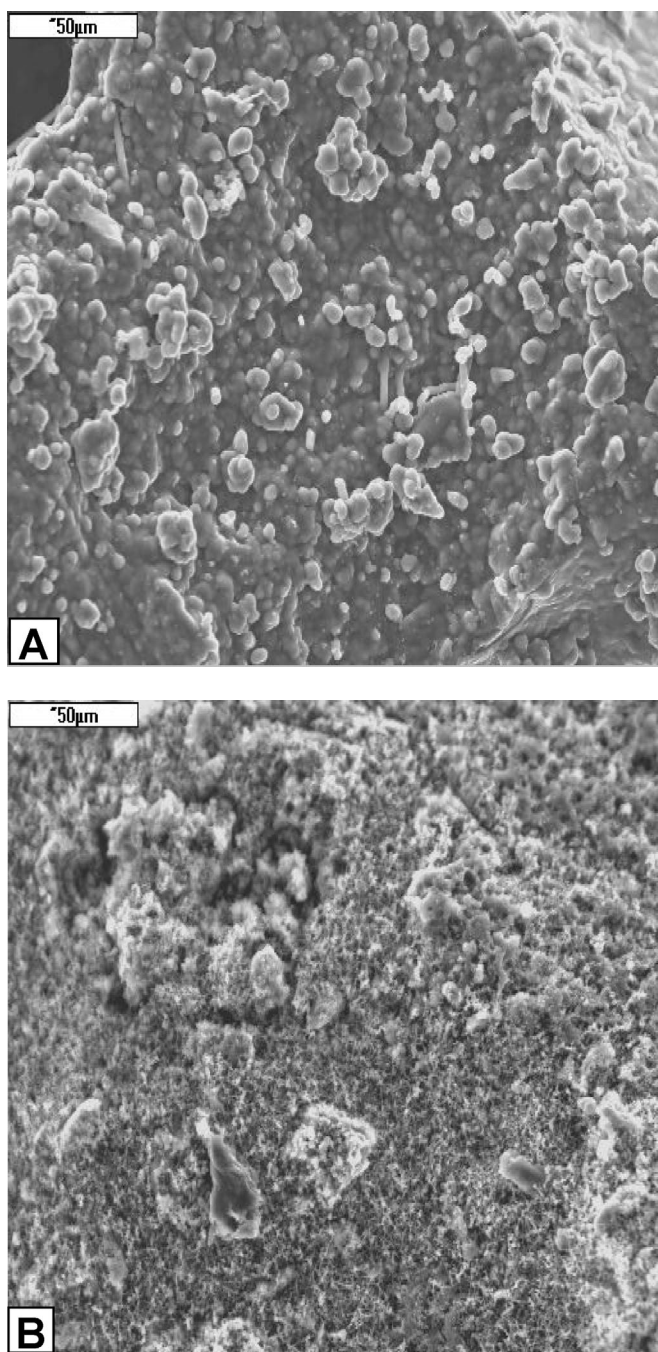
Figure 1. SEM images illustrating surface development for C/SiC composites obtained from the pitch/SiO_2 system at applied carbonization temperatures: (A) 1300°C; (B) 1650°C.
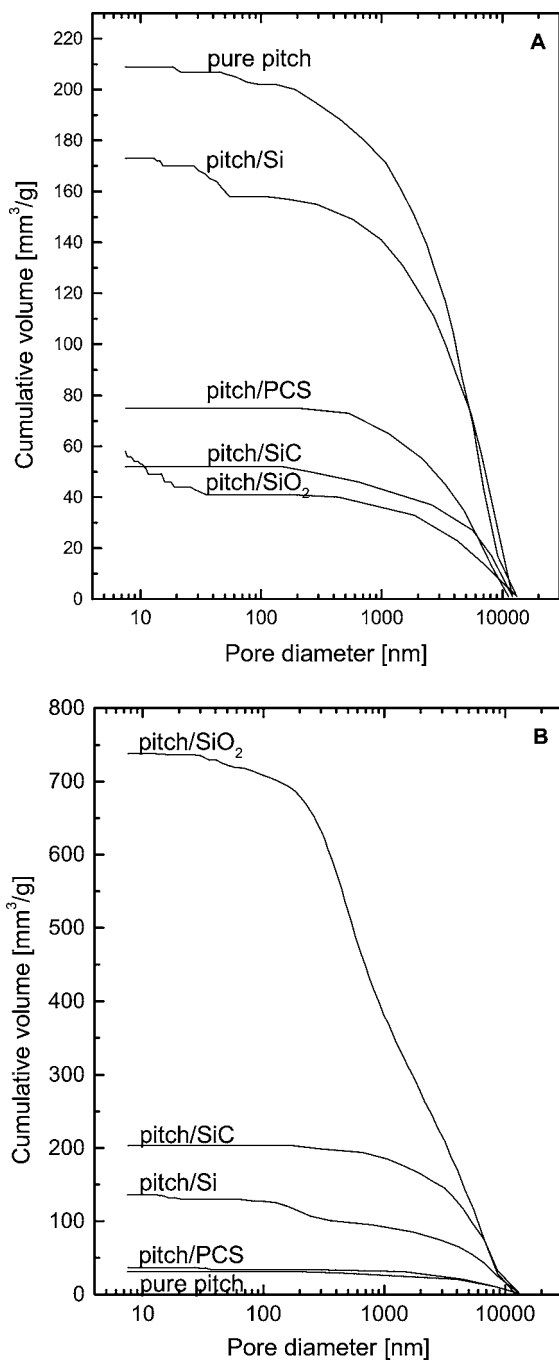
Figure 2. Cumulative pore volumes from mercury porosimetry for carbonizates from the indicated reaction systems: (A) 1300°C; (B) 1650°C. PCS is an abbreviation for poly(carbomethylsilane).

Si, pitch/poly(carbomethylsilane)) precursor species contributing their own low porosities to the overall sample porosity and, therefore, showing overall lower porosities compared with the nonmodified carbonizate.

The results in Fig. 2B for the 1650°C carbonizates clearly indicate a dramatically different sequence of the porosity curves than discussed above. The highest porosity is now found for the composite from the pitch/SiO$_2$ system, a ten-fold increase compared with the relevant product from the 1300°C stage. This observation can likely be linked to the major chemical reaction at the higher temperature, i.e. carbothermal reduction of silica and the evolution of new pores and possible expansion of the existing ones as previously mentioned when discussing the BET data.

For the pitch/SiC system, an increase in porosity after the 1650°C pyrolysis can also be linked to volume-related effects due to the carbothermal reduction of passivating SiO$_2$ layers and formation of secondary SiC. Additionally for this system, differences in thermal expansion coefficients between the carbon phase and SiC grains at phase boundaries may contribute to unfavourable mechanical strain and evolution of microcracks on cooling.

Some typical SEM images for the 1300°C composite systems are displayed in Fig. 3. The pictures were taken for bigger samples of materials, approx. 10 mm in size, that were preserved (not ground) after the 500°C initial carbonization so to enable microscopic observations of evolving macro-morphological features. These specimens were further pyrolyzed at increased temperatures together with the parent bulk powder to yield the actual samples for SEM examination. For example, Fig. 3A shows an image for the system pitch/Si with abundant macropores developed in the massive body of the composite's solid matrix. Figures 3B and 3C represent images for the pitch/SiO$_2$ and pitch/commercial SiC systems, respectively, that are characteristic of, generally, fewer macropores than observed in the previous pitch/Si system. This likely results from the lack of significant chemical changes in the former systems wherein the silicon precursors are mostly inert, while in the latter one the elemental silicon is shown to react toward detectable nano-SiC under the applied conditions [20]. On the other hand, the respective material from the pitch/poly(carbomethylsilane) system (Fig. 3D) appears to contain even more macropores forming a foam-like structure of the matrix. In conclusion, the images support qualitatively the conclusions from the porosimetry and BET studies about the prevailing meso- and macroporous nature of these solids.

Typical SEM images and the matching maps of element distribution (C carbon, O oxygen, Si silicon) obtained for the 1650°C carbonizates from the pitch/elemental Si and pitch/commercial SiC systems are included in Fig. 4, part A and part B, respectively. A characteristic feature of the images for the pitch/Si system is a uniform distribution of all the mapped elements supporting, first, a very efficient mixing of components and, second, an advantageous uniform distribution of the resultant nano-SiC in the carbon matrix evolved from the pitch (Fig. 4A). This is also true for the pitch/SiO$_2$ and pitch/poly(carbomethylsilane) systems (not shown).
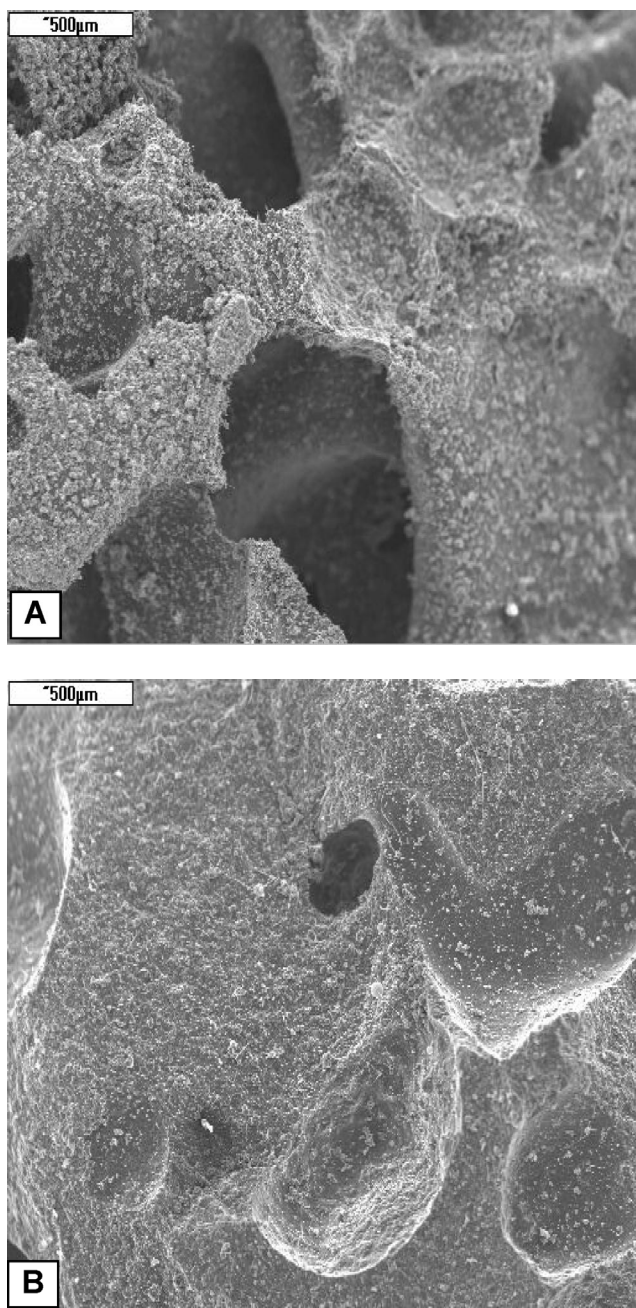
Figure 3. SEM images for carbonizates obtained at 1300°C under an argon atmosphere from the systems: (A) pitch/elemental Si; (B) pitch/SiO$_2$; (C) pitch/commercial SiC; (D) pitch/poly(carbomethylsilane).
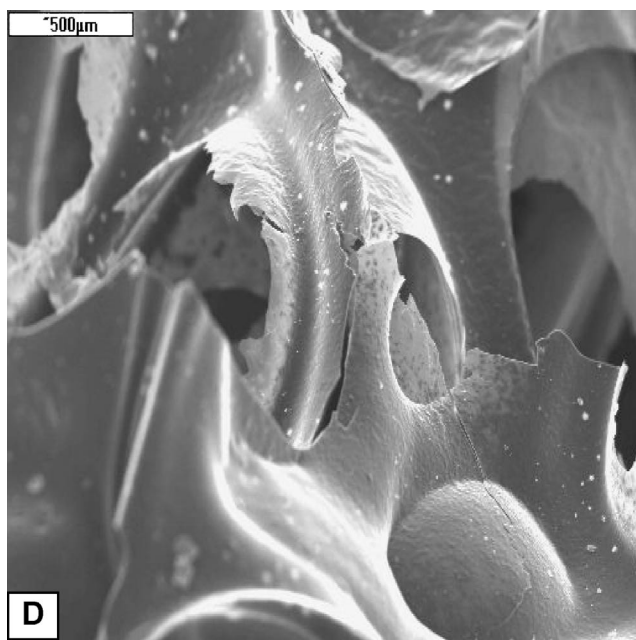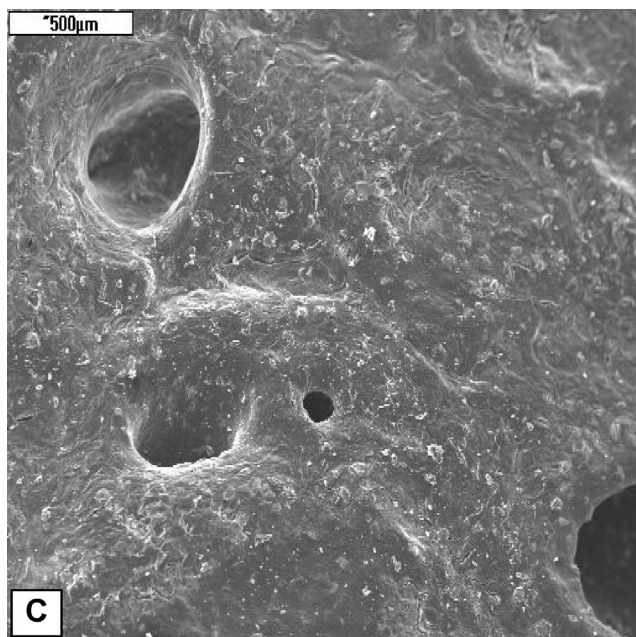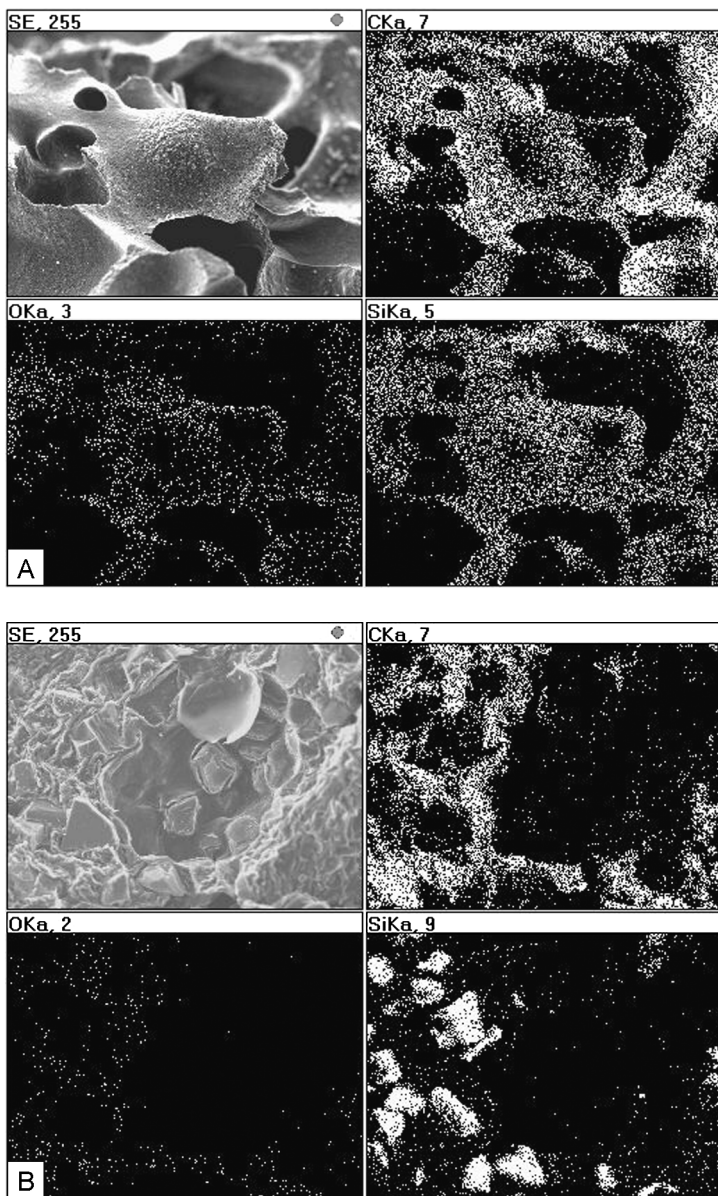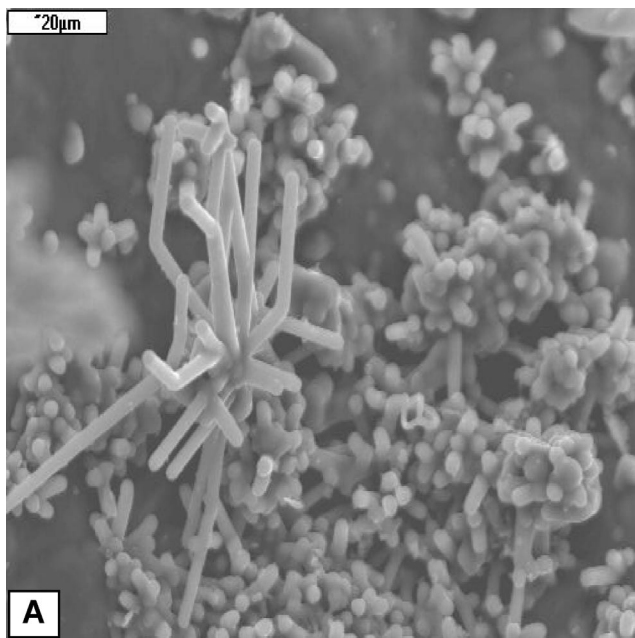
Figure 3. (Continued).

Figure 4. SEM images and corresponding maps of element distrubutions in carbonizates obtained at 1650°C under an argon flow from the systems: (A) pitch/elemental Si; (B) pitch/commercial SiC. SEM image — upper left corner; C distribution — upper right corner; O distribution — bottom left corner; Si distribution — bottom right corner.

On the other hand, the maps collected for the reference pitch/SiC system (Fig. 4B) clearly support the existence of separate, relatively large grains of SiC which, due to their overall chemical inertness during carbonization, persisted throughout the

treatment seemingly unchanged in bulk. In this regard, it is worth recalling that a detailed insight into this system supported carbothermal reduction within the passivating SiO_2 layers of the component's grains and the formation of secondary nano-SiC [20].

An interesting microscopic feature was observed for all systems but the pitch/commercial SiC carbonized at 1300°C, namely, the occurrence of numerous whiskers found both on flat surfaces and in big open pores of the more massive samples (Fig. 5). The whiskers were confirmed by EDX mapping to be forms of silicon carbide materials. The formation of SiC whiskers is generally thought to proceed *via* participation of reactive volatile silicon species in the gas phase, thus indicating yet another reaction pathway operating in these systems [25, 26]. The extent of whisker formation seemed to be connected with amounts of available oxygen and it was a rather peripheral phenomenon under applied conditions. In this regard, no whiskers were observed in the related bulk powdered samples supporting a view that their formation is additionally governed by local mass transport and diffusion phenomena. Finally, abundant SiC whiskers were also seen in the pitch/SiO_2 system after the 1650°C pyrolysis consistent with the efficient carbothermal reduction chemistry taking place in this temperature range.

Figure 5. SEM images of whisker features found in carbonizates obtained at 1300°C under an argon atmosphere from the systems: (A) pitch/elemental Si; (B) pitch/SiO_2; (C) pitch/poly(carbomethylsilane).
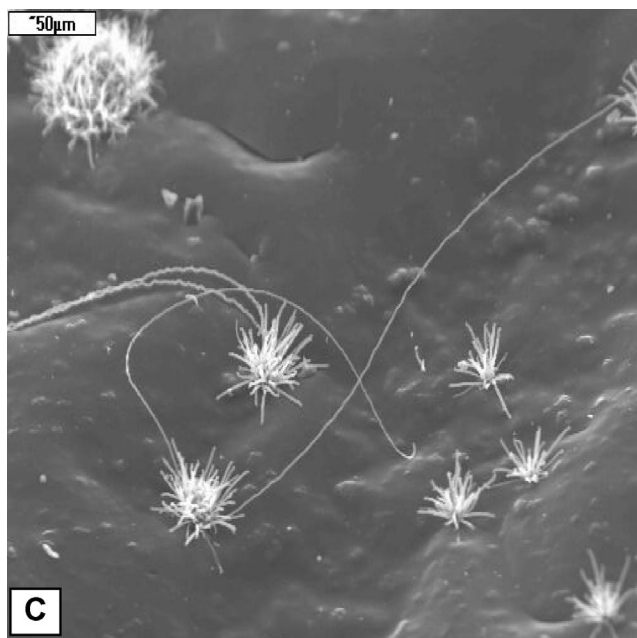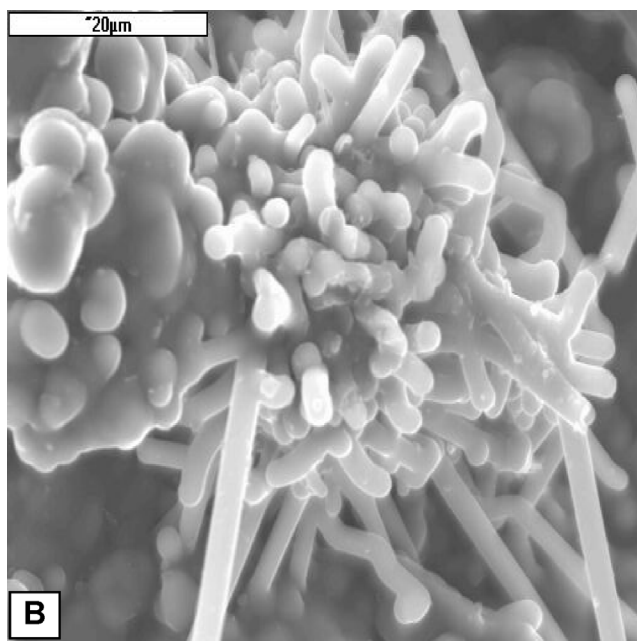
Figure 5. (Continued).

4. CONCLUSIONS

We successfully prepared homogeneously dispersed binary mixtures of a coal tar pitch with individual powdered silicon additives for stepwise carbonization of the systems up to 1650°C, under an argon flow, to yield nanocomposite products C/SiC.

Some specific reaction pathways were observed in the pitch/elemental Si, pitch/SiO_2, and pitch/poly(carbomethylsilane) systems resulting in occasional SiC whisker formation.

All products were found to show relatively small BET surface areas determined by low-temperature adsorption of nitrogen, but with some differences that could be traced to specific chemical changes in the systems.

The porosimetry results supported the prevailingly meso- and macroporous nature of the materials with strong temperature dependence of the size of porosity. For instance, in the pitch/SiO_2 system, the overall porosity of the 1650°C carbonizate was ten times larger than the respective value for the 1300°C carbonizate. Such variations were linked to the mass transport/temperature specifics of the carbothermal reduction of silica taking place in this temperature range.

The majority of the nanocomposites showed comparable helium densities except for the pitch/poly(carbomethylsilane) system in which the densities of the products were significantly lower suggesting abundant closed pores and resulting in a unique composite material.

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