Available online at www.sciencedirect.com
SCIENCE DIRECT®
Microelectronic Engineering 81 (2005) 353–357
MICROELECTRONIC ENGINEERING
www.elsevier.com/locate/mee

The effect of precursor system on the resistivity and oxidation susceptibility of C/SiC nanocomposites en route to electronic grade nanomaterials

Cezary Czosnek, Mariusz Drygaś, Jerzy F. Janik *

AGH University of Science and Technology, Faculty of Fuels and Energy, Al. Mickiewicza 30, 30-059 Kraków, Poland

Dedicated to honor Professor Aleksander Karcz on the occasion of his 65th birthday. Sto lat!

Abstract

Presented are results of a study on specific technological properties of affordable C/SiC composite nanomaterials obtained via pyrolysis of several pitch/silicon-bearing precursor systems (elemental Si, silica SiO_2, poly(carbomethylsilane) $[–CH_2–Si(H)CH_3–]_n$, commercial SiC). For pyrolysis at 1300 °C, the formation of nanosized SiC is detected in the systems with elemental Si and poly(carbomethylsilane) while 1650 °C pyrolysis is required for silica to achieve such conversion. In situ formed nano-SiC is homogeneously dispersed in the simultaneously evolving graphitic carbon matrix of the composites. Reactivities vs. CO_2, electrical resistivities, and surface properties of the nanocomposites are determined. Significant differences and patterns in the properties among the materials obtained from these precursor systems and at the selected pyrolysis temperatures are clearly established. Among others, the data suggest potential for carbon removal from the most reactive nanocomposites via reactions with CO_2 to yield unique nano-SiC powder products for further processing towards electronic and ceramic applications.

Keywords: Coal tar pitch; Silicon carbide; SiC; Nanomaterials; Nanocrystalline; Composites

---

1. Introduction

Silicon carbide SiC thanks to its advantageous mechanical, thermal, and electrical properties has found numerous applications. It has been extensively used in modern electronics to make artifacts designed to work at increased temperatures and/or under high voltage and high AC frequencies where it often supercedes elemental silicon Si [1]. Both silicon and silicon carbide are known to get oxidized under suitable conditions to thermally stable silicon dioxide SiO_2 (silica) and their

---

* Corresponding author. Tel.: +48 12 617 2577; fax: +48 12 617 2066.
E-mail address: janikj@uci.agh.edu.pl (J.F. Janik).

0167-9317/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2005.03.031

grains are always covered by thin compact films made of Si–O moieties. This is especially true with nanocrystalline forms of SiC that under oxidizing conditions become easily coated with the oxide layer, compared with somewhat more robust monocrystalline SiC, resulting in electrically negative character of the oxidized surface layer that may improve the electric field distribution at the edge of power devices. Also, SiC has been considered in composite materials for construction of nuclear reactors and various reactors' linings [2,3].

Traditional ways to synthesize bulk SiC rely on thermochemical reactions between elemental Si or SiO_2 and solid sources of carbon C. Plausible carbon sources also include coal tar pitches with low softening points which are complex mixtures of hydrocarbons with a range of molecular make-up that are usually much more reactive toward silicon precursors than solid carbons. Other available routes to bulk SiC depend on pyrolytic decomposition of single-source precursors such as carbosilane and carbosiloxane polymers or even biomass containing silicon-bearing components. For example, the latter source enables at relatively low temperatures the preparation of nano-SiC powders that may, subsequently, be used in sintering/grain growth processes to yield ceramic composites with tailored microstructures [4,5] and advantageous mechanical features due to high grain boundary strength [6].

Herein, presented is a study aimed at appraising several "practical" properties of nanocomposites C/SiC prepared via pyrolysis of mixtures made of various silicon-bearing precursors and a coal tar pitch (reactive and affordable source of C), mainly, the composites suitability for making pure nanopowders of SiC by controlled oxidation/removal of the carbon component.

2. Experimental

The final composites C/SiC were prepared by pyrolysis under an argon atmosphere of the initial solid carbonizates obtained at 500 °C that were, subsequently, treated for 1 h at 1300 or 1650 °C. Each initial carbonizate was made from a thoroughly homogenized mixture of a coal tar pitch and a selected silicon-bearing additive (15 wt%). Reference carbonizates were also made at the two final temperatures from a non-modified (pure) pitch. The silicon-bearing precursors included elemental Si, silica SiO_2, poly(carbomethylsilane) (PCS), and commercial SiC as yet another reference system. The starting mixtures were first appropriately homogenized as powdered solids followed by stirring in a liquid medium of a molten pitch at 160 °C. The detailed descriptions of the procedures and characterization data for these systems have already been published [7–9].

Herein, the nanocomposites C/SiC that contained free carbon were subjected to investigations of their suitability to oxidation under a CO_2 atmosphere by determinations of the reactivity indices R characterizing a propensity of the carbon component toward mild oxidation with CO_2 [10]. In this method, two grams of a 0.2–0.4 mm grain size fraction of a material are placed in a quartz tube and heated to 1000 °C while being purged by a 3 cm^3/s stream of CO_2 at a constant pressure of 101.325 kPa. The carbon dioxide gas passes through the material's bed of which temperature is continuously measured by a thermocouple. The content/concentration of CO in the off-gas is recorded by an analyzer and used to calculate the reactivity index R ($cm^3/g \cdot s$). In general, the bigger is the index the higher is the material's reactivity. Electrical resistivities of the powder materials were determined with a home-made apparatus based on the methodology described in Polish Standard BN 77/0511-30. The apparatus consists of a cylindrical volume bored in an insulating body and equipped with two fitted copper pistons. One of the pistons is able to move inside the cylinder and, therefore, used to make compacts of the powders. Both pistons are connected by electrical cables to an electronic set-up and also serve as "points" for measurements of electric voltage gradients. The resistivities are derived from measurements of the current and voltage gradient, the latter resulting from the resistance and geometrical constraints of the sample in the cylinder according to: $r = U \cdot S/I \cdot L$, where r is the resistivity, U the voltage gradient, S the cross-sectional area of the sample, I the current, and L the distance between the pistons (length of sample). All determinations were carried out under identical conditions including applications of the same compacting force.

3. Results and discussion

The reactivity and electrical resistivity indices along with the data on helium densities and BET surface areas determined for the composites and reference materials are presented in Table 1. Two types of reference materials were prepared including the non-modified carbonizates derived from a pure pitch and composites from the system pitch/commercial SiC both after the 1300 and 1650 °C treatments. At this point, it is useful to recall that our previous studies on the formation of SiC in these systems point out to its evolution already at 1300 °C in the systems with elemental Si and PCS while treatments at 1650 °C were necessary in the system pitch/SiO_2 and with other related Si–O group containing precursors [7–9,11].

The current data for the 1300 °C carbonizates indicate that the highest reactivity indices are found for the non-modified carbonizate and for the composite from the system pitch/PCS. A significantly lower value is obtained for the comparable composite in the system pitch/elemental Si. On the other hand, the composites from the two remaining systems in which the silicon precursors are mostly chemically unchanged after this treatment, i.e., pitch/SiO_2 and pitch/commercial SiC, are characterized by comparable indices that are about half of the reactivity index value for the reference non-modified carbonizate. This can be interpreted in terms of the propensity of materials for free carbon oxidation/removal. Therefore, the composite from the system pitch/elemental Si is the most robust and less reactive than the non-modified carbonizate while the one from the system pitch/PCS is the least resistant to oxidation under applied conditions. In this regard, it is worth mentioning that CO_2 interacts with free carbon on accessible pore surfaces according to the Boudouard's reaction

$$CO_2(g) + C(s) \leftrightarrow 2CO(g) \quad (1)$$

while silicon carbide of which presence was confirmed by XRD in the 1300 °C composites from the systems with elemental Si and PCS but not with SiO_2 [7] is not expected to appreciably react with CO_2 at 1000 °C, the temperature applied in the reactivity determinations [12].

The relatively low reactivity indices for the 1300 °C carbonizates from the individual systems pitch/elemental Si, SiO_2, and commercial SiC may likely result from the formation of surface species SiO_xC_y via chemical interactions of the precursors with the evolving carbon matrix. In this regard, on the one hand, both elemental Si and commercial SiC grain surfaces are covered with protective layers of SiO_2 and, on the other hand, there are reactive oxygen-bearing pitch components that all could be the source of oxygen toward the formation of such unreactive/protective species. The SiO_xC_y linkages are known to resist oxidation up to 1400 °C [13,14] and, therefore, could contribute to enhanced oxidation resistance in the composite system with carbon [15].

Table 1
Characteristics of the composites C/SiC and reference carbonizates

Sample	d_{He} (g/cm^3)		S_{BET} (m^2/g)		Reactivity Index R_{CO2} (cm^3/g · s)		Resistivity (Ω · cm)	
	1300 °C	1650 °C	1300 °C	1650 °C	1300 °C	1650 °C	1300 °C	1650 °C
A	2.15	2.43	1.4	2.0	0.08	0.33	0.22	0.18
B	2.18	2.44	4.0	8.3	0.18	0.76	0.16	0.63
C	2.28	2.37	0.4	1.2	0.17	0.30	0.10	0.08
D	1.83	1.76	1.3	1.9	0.42	0.27	0.29	0.02
E	2.04	2.09	1.4	0.7	0.30	0.16	0.05	0.05

Note: samples (carbonizates) obtained from different precursor systems are labeled as follows: A, pitch/elemental Si; B, pitch/SiO_2 (silica); C, pitch/commercial SiC; D, pitch/poly(carbomethylsilane) (PCS); E, non-modified pitch.

Among the 1650 °C carbonizates, the one from the system pitch/SiO_2 shows an outstandingly high reactivity index that can be linked to the composite's highest BET surface area as a decisive factor influencing its reactivity. All the remaining composites show similar alas higher reactivities than the reference non-modified carbonizate. The generally higher and rather unexpected reactivities of the 1650 °C composites compared to the relevant non-modified carbonizate might be explained by superimposition of two opposite effects: first, an intrinsically increased crystalline ordering of carbon matrix toward a graphite structure at higher temperatures and, second, an increased pore surface at grain boundaries due to efficient thermochemical reactions between the carbon matrix and the silicon-bearing additives often associated with massive gas evolution.

As far as the first factor is concerned, increasing ordering of graphitic domains of the carbon matrix should result in an improved oxidation resistance (lower oxidation reactivities) of the materials. In this regard, our XRD study clearly indicated that, other things being equal, the 1650 °C composites showed inferior crystalline ordering of the C-lattice relative to the reference non-modified carbonizate [7]. Looking at the second factor, one should expect a positive correlation between the grain surface area/number of active centers and reactivity toward oxidation [16]. The BET surface areas of the 1650 °C materials, S_{BET}, show that the lowest value is found for the non-modified carbonizate to be compared with its lowest reactivity index. Apparently, in this case both factors add synergistically causing the carbonizate to be the least reactive toward oxidation.

The highest reactivity among the 1650 °C materials is exhibited by the composite from the system pitch/SiO_2 that, at the same time, has the highest BET surface area. The latter observation is consistent with the completion of carbothermal reduction of silica at this temperature according to the overall reaction

$$SiO_2(s) + 3C(s) \leftrightarrow SiC(s) + 2CO(g) \tag{2}$$

In the initial stage, SiO_2 presumably reacts with C to yield the following gaseous by-products

$$SiO_2(s) + C(s) \leftrightarrow SiO(g) + CO(g) \tag{3}$$

while the resulting CO gas reacts further with available silica

$$SiO_2(s) + CO(g) \leftrightarrow SiO(g) + CO_2(g) \tag{4}$$

The carbon dioxide is then involved in the equilibrium with CO and C (reaction 1) and, subsequently, silicon carbide is mainly formed from

$$SiO(g) + 2C(s) \leftrightarrow SiC(s) + CO(g) \tag{5}$$

It worth noting that the formation of solid SiC is accompanied by the evolution of significant gaseous species CO/CO_2 leaving the reaction system with the purging argon gas. The net effect, therefore, is the enhancement/enlargement of pore surface area both due to the reaction-promoted evolution of inter-grain surfaces and, possibly, opening of closed pores.

The results on electrical resistivity in Table 1 show that, generally, the resistivities of all the Si-modified composites are higher than the resistivities of the reference non-modified carbonizates. This can likely be linked to the fact that both the pure silicon-bearing precursors and SiC are known to have higher resistivities than the comparable pure carbonizates obtained from the pitch. However, other factors such as quantities and characteristics of inter-grain surface contacts and their chemical nature (aspects not investigated in this study) are anticipated to play an important role, too. Among the 1300 °C materials the composite from the system pitch/PCS has the highest resistivity while after the 1650 °C treatment the highest resistivity is found for the composite from the system pitch/SiO_2.

Comparing the 1300 and 1650 °C materials, it is found that the increased structural ordering of the graphitic carbon matrix appears to be a rather insignificant factor in the materials resistivities determined by the applied method. It is more the specifics of chemical conversion and presence of the silicon-bearing species dispersed in the carbon matrix that are responsible for the observed trends in the composites' resistivities. For example, the drastic almost threefold increase of the resistivity for such a pair of composites in the system pitch/SiO_2 seems, likely, to result from the carbothermal reduction of silica accompanied by massive gas evolution, loss of carbon, and increased pore surface area – the phenomena that significantly alter amounts and nature of inter-grain connectivities.

4. Conclusions

The composites C/SiC obtained from the selected precursor systems are characterized by homogeneous distribution of SiC nano-grains in the graphitic carbon matrix. The composites are found to display the diversified electrical resistivities apparently resulting from the specifics of the precursor routes. For example, the resistivity of the 1650 °C composite from the system pitch/poly(carbomethylsilane) is comparable with the resistivity for the reference non-modified carbonizate which implies that, in this case, the presence of well dispersed nanocrystalline grains of SiC does not negatively impact on this property while modifying other materials features. The outstandingly high resistivities observed in the system pitch/SiO_2 that is characterized by high mass transport reaction chemistry point out to the essential role of inter-grain surface evolution/grain connectivities evolved during composite preparation in electric current conductivities of such powder materials.

The composite materials with a range of reactivities toward oxidation are obtained encompassing products some of which are thermally and chemically robust and others that are prone to reactions with CO_2. The latter composites can in principle be used, upon feasible removal of excess free carbon, to make powders of pure nanocrystalline SiC. Especially, well suited for this purpose appear to be the low density 1300 °C composite from the system pitch/poly(carbomethylsilane) and 1650 °C composite from the system pitch/SiO_2.

The composites prepared from the system pitch/poly(carbomethylsilane) are characterized by the outstandingly low helium densities that are even lower than the densities for the reference non-modified carbonizates. Such low density C/SiC materials with improved chemical resistance can be considered for applications as advantageous thermal insulation, catalytic support or filtration modified carbons.

Further studies aimed at optimization of composites make-up and controlled oxidation with CO_2 or air toward pure nanocrystalline SiC are on the way and their results will be published elsewhere.

Acknowledgment

This work was supported by AGH University of Science and Technology Grant No. 11.11.210.62.

References

[1] C. Raynaud, J. Non-Cryst. Solids 280 (2001) 1–31.
[2] Y. Zhang, W.J. Weber, C.M. Wang, Phys. Rev. B 69 (2004) 205201 (1–9).
[3] L. Giancarli, J.P. Bonal, A. Caso, G. Le Marois, N.B. Morley, J.F. Salavy, Fusion Eng. Des. 41 (1998) 165–171.
[4] Z. Shen, H. Peng, J. Liu, M. Nygren, J. Eur. Ceram. Soc. 24 (2004) 3447–3452.
[5] H.-J. Choi, Y.-W. Kim, M. Mitomo, T. Nishimura, J.-H. Lee, D.-Y. Kim, Scripta Mater. 50 (2004) 1203–1207.
[6] A. Bellosi, D. Sciti, S. Guicciardi, J. Eur. Ceram. Soc. 24 (2004) 3295–3302.
[7] C. Czosnek, W. Ratuszek, J.F. Janik, Z. Olejniczak, Fuel Process. Technol. 79 (2002) 199–206.
[8] C. Czosnek, J.F. Janik, Z. Olejniczak, J. Cluster Sci. 13 (2002) 487–502.
[9] C. Czosnek, Conversions of elemental silicon and its compounds during copyrolysis with a pitch from the point of view of product characteristics modifications, PhD Dissertation, AGH University of Science and Technology, Kraków, Poland, 2003 (in Polish).
[10] Polish Standard PN 90/C-04311 (in Polish).
[11] C. Czosnek, J. Wolszczak, M. Drygaś, M. Góra, J.F. Janik, J. Phys. Chem. Solids 65 (2004) 647–653.
[12] M. Balat, R. Berjoan, G. Pichelin, D. Rochman, Appl. Surf. Sci. 133 (1998) 115–123.
[13] Q. Wei, E. Pippel, J. Woltersdorf, M. Scheffler, P. Greil, Mater. Chem. Phys. 73 (2002) 281–289.
[14] C.G. Pantano, A.K. Singh, H. Zhang, J. Sol–Gel Sci. Technol. 14 (1999) 7–25.
[15] L.M. Manocha, S. Manocha, K.B. Patel, P. Glogar, Carbon 38 (2000) 1481–1491.
[16] P. Ehrburger, F. Louys, J. Lahaye, Carbon 27 (1989) 389–393.