

OXYCARBIDE-DERIVED CARBON (OCDC): A NOVEL FORM OF HIGHLY POROUS CARBON

Gian D. Soraru¹, P. R. Aravind¹, Raquel Pena-Alonso² and Hans-Joachim Kleebe²

¹Department of Materials Engineering, University of Trento, Italy and

²Institute for Applied Geosciences, Technische Universität Darmstadt, Germany.

Introduction

Pyrolysis in inert atmosphere of siloxane polymers of hybrid silica gels leads to a new class of C-containing materials, named silicon oxycarbide glasses (SiCO) [1]. They belong to the broader family of Polymer-Derived Ceramics, PDC [2]. The SiCO nanostructure is formed by silica nanodomains surrounded by domain walls that are built up by graphene sheets which are connected to each other *via* SiC nanocrystals [3]. The interface between the silica domains and the graphene sheets/SiC nanocrystals contains mixed oxycarbide units. It has been shown that the silica nanodomains can be etched by hydrofluoric acid [4] and this treatment leaves behind a novel form of porous carbon-based material, namely a nanoporous oxycarbide-derived carbon (OCDC). In this study we'll show that it is possible to control the microstructure of the OCDC (pore volume and size, specific surface area) through the chemistry of the siloxane precursor as well as the pyrolysis conditions (maximum temperature and time) of the parent SiCO glass.

Experimental

SiCO and SiBOC samples were prepared by the sol-gel method using methyltriethoxysilane (MTES) and boric acid, following a procedure reported elsewhere [5]. MTES was purchased from ABCR (Germany) and B(OH)₃ from Carlo Erba (Italy) and both reagents were used as received. The SiBOC gel had a B/Si = 0,2 (atom. ratio). Gels were dried at 70 °C for at least 10 days. SiOC and SiBOC glasses were obtained from gel fragments, with a pyrolysis process under flowing Ar (100 mL/min) at 5 °C/min up to 1200, 1400, and 1500 °C for 1 h. In order to follow the structural evolution as a function of the annealing time pyrolysis treatments were performed at 1400°C for 1, 3, 5 and 10 h. The etching process was performed on 0.5 g of 80-120 μm sieved oxycarbide powders using an HF (20 vol% in H₂O) solution [4]. SiOC and SiBOC glasses were characterized before and after etching by chemical analysis, XRD, nitrogen gas adsorption (BET method), and HR-TEM. Chemical analysis was performed by the Service Central d'Analyse du CNRS, Vernaison, France. Si, C, B, and H were measured. O was estimated by difference to 100%. X-ray diffractograms were collected on a Rigaku Dmax diffractometer in the Bragg-Brentano configuration using Cu KR radiation, operating at 40 kV and 30 mA. The N₂ adsorption isotherms were collected at 77 K using an ASAP 2010 (Micromeritics, Gemini Model 2010, USA). The specific surface area was determined using the BET equation with an accuracy of ±10 m²/g. The pore size distribution was obtained

using the Barrette-Joynere-Halenda (BJH) method. The microprobe volume was determined by Harkins-Jura method. Micro/nanostructural characterization of the HF etched and annealed samples was performed by TEM using a FEI CM20STEM instrument, operating at 20 keV (Eindhoven, The Netherlands). TEM sample preparation followed standard techniques for ceramic compound; grinding, dimpling, Ar-ion milling followed by light carbon coating to minimize charging under the incident electron beam.

Results and Discussion

CA analysis performed on selected samples is reported in Table 1.

Table 1. Chemical analysis of selected samples at 1400 °C.

Sample	Composition (wt%)				
	Si	B	C	H	O
SiOC, 1h	46,2	--	14,5	<0,3	39,4
SiOC, 1h HF	35,2	--	34,2	1,3	29,4
SiBOC, 1h	41,0	3,2	11,8	<0,3	44,1
SiBOC, 1h HF	26,3	1,8	33,0	1,7	37,2
SiBOC, 10h	42,0	3,2	12,0	<1,3	42,6

It can be noted that the samples after the etching process are depleted in Si, O and B and are enriched in C confirming that HF removes only the oxidic fraction but do not attack the Si-C and B-C bonds. Chemical composition does not change after 10 hours annealing at 1400°C confirming that the SiBOC glasses are stable at high temperature [6] and that the rearrangement of the glass network which takes place above 1200 °C occurs without decomposition and weight loss.

The spectrum of the SiOC and SiBOC samples pyrolyzed at 1200 °C show a completely amorphous structure with only the presence of the silica halo centered at about $2\theta = 22^\circ$. The increase of the pyrolysis temperature promotes a phase separation into a silica-rich and SiC rich phases with the crystallization of β -SiC as revealed by broad peaks at 35, 60 and 72°. In the B-containing samples the crystallization process is faster leading to slightly larger SiC nanocrystals. The continuous silica-based network can be removed by the HF etching. Consequently, in the XRD spectra of the HF treated samples the silica halo at $2\theta = 22^\circ$ progressively decreases with increasing the maximum temperature allowing the reflections associated to the crystalline phases present in these glasses (SiC and graphite) to emerge and to become, at 1500 °C, the only diffraction peaks.

Nitrogen adsorption analysis gave the results in Table 2.

The pore volumes increase with the pyrolysis temperature while the SSA is in the range 500-570 m²/g. By comparing the data of SiOC and SiBOC for the same pyrolysis conditions we can see that SiBOC glasses develop more porosity and larger pore sizes than the B-free SiOC. The adsorption-desorption isotherms collected on the OCDCs obtained during the isothermal treatment at 1400°C are shown in **Figure 1** and can be classified as Type IV according to the IUPAC nomenclature. At higher pressure samples annealed for more

than 1 hour clearly show a hysteresis loop which is caused by the capillary condensation in the mesopores.

Table 2. N₂ adsorption analysis results performed on selected samples.

Sample	SSA (m ² /g)	Mesoporous volume (cm ³ /g)	Micropore Volume (cm ³ /g)
SiOC, 1400 °C, 1h	482	0.14	0.26
SiOC, 1500 °C, 1h	562	0.23	0.33
SiBOC, 1400 °C, 1h	567	0.12	0.30
SiBOC, 1400 °C, 3h	570	0.46	0.35
SiBOC, 1400 °C, 5h	533	0.45	0.37
SiBOC, 1400 °C, 10h	524	0.58	0.39
SiBOC, 1500 °C, 1h	539	0.66	0.54

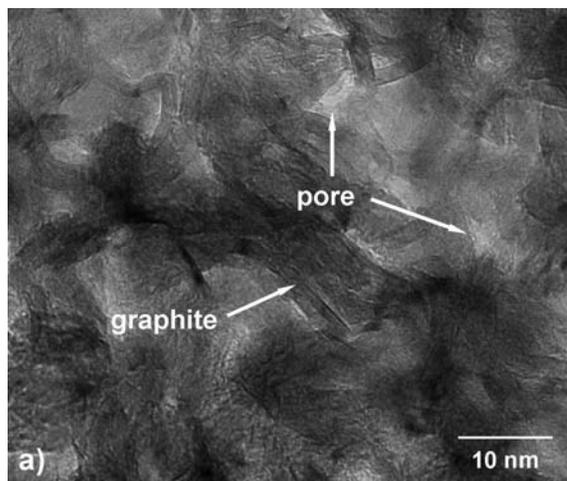


Fig. 2. HR-TEM of the OCDC obtained after 10 h at 1400 °C.

Conclusion

The effect of: (i) the chemistry of siloxane precursor, (ii) the maximum pyrolysis temperature and (iii) the annealing time on the nanostructural development of porous OCDCs were investigated. We have shown that the amount of porosity and the pore size both increase with the maximum pyrolysis temperature and time. Moreover, B-addition leads to a faster phase separation of the parent silicon oxycarbide glass thereby increasing the porosity and the pore size of the resulting OCDCs. This novel form of porous carbon is currently investigated as H₂ storage material and as anode for Li ion batteries.

Acknowledgments. The authors acknowledge the financial help from Provincia Autonoma di Trento under the project NAOMI and the European Community, through a Marie Curie Research and Training Network “PolyCerNet” (<http://www.ing.unitn.it/~soraru/>), MRTN-CT-019601

References

- [1] Renlund GM, Prochaszka S, Doremus RH. Silicon oxycarbide glasses: Part I. Preparation and chemistry. *J Mater Res* 1991; 6:2716-2722.
- [2] *Polymer Derived Ceramics: From Nanostructure to Applications*, Ed. By P. Colombo, R. Riedel, G. D. Sorarù, H.-J. Kleebe, DEStech Publications, Inc. (September 28, 2009), Lancaster, USA, (2009).
- [3] Saha A, Raj R, Williamson DL. A Model for the Nanodomains in Polymer-Derived SiCO. *J Am Ceram Soc* 2006; 89(7):2188–2195.
- [4] Pena-Alonso R, Raj R, Soraru GD. Preparation of Ultrathin-Walled Carbon-Based Nanoporous Structures by Etching Pseudo-Amorphous Silicon Oxycarbide Ceramics. *J Am Ceram Soc* 2006; 89(8):2473–2480.
- [5] Pena-Alonso R, Mariotto G, Gervais C, Babonneau F, Soraru GD. New Insights on the High-Temperature Nanostructure Evolution of SiOC and B-Doped SiBOC Polymer-Derived Glasses. *Chem Mater* 2007; 19:5694-5702.
- [6] Schiavon MA, Gervais C, Babonneau F, Soraru GD, Crystallization Behaviour of Novel Silicon-Boron-Oxycarbide Glasses. *J Am Ceram Soc* 2004; 87(2):203–208.

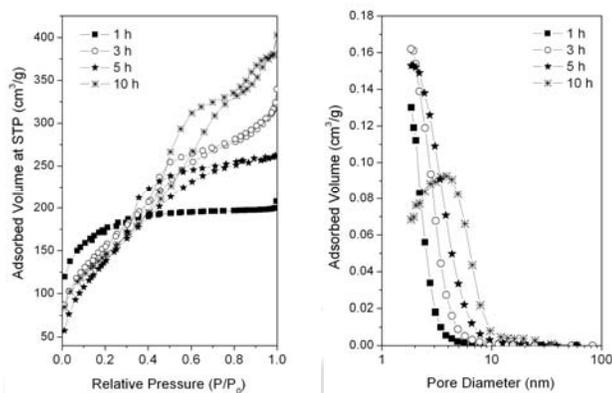


Fig. 1. Adsorption-Desorption Isotherms and Pore size Distribution of the OCDCs as a function of annealing time at 1400 °C

The sample with the longest annealing time (10 h) even shows a second hysteresis loop close to the saturation pressure. At lower pressures ($p/p_0 < 0.04$) the isotherms are not linear which indicates the presence of micropores in the material. The amount of adsorbed nitrogen increases with the annealing time, suggesting that the pore volume is also increasing. The pore size distribution of the OCDC samples is shown in **Figure 2**. From these data it is clear that the pore volume and pore size of the OCDC continuously increases with the annealing time of the parent SiBOC glass. After 10 hours the pore size distribution curve shows a maximum between 4 and 5 nm while for 1, 3 and 5 h annealing, even if the curves continuously shift towards larger pores, the maximum of the pore size distribution curves remains < 2 nm.

The evolution of the total porosity, as recorded by BET analysis, is consistent with the TEM observations. Figure 2 reveals the nanostructure upon annealing for 10 hours at 1400 °C. TEM images clearly shows the pore size up to 5 nm. It is worth noting that while upon annealing for 1 hour predominantly turbostratic carbon was observed, the maximum heat treatment for 10 h at 1400 °C resulted in the formation of graphitic carbon.