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The effect of annealing at 1400 °C on the structural evolution of porous C-rich silicon (boron)oxycarbide glass

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Abstract

A precursor SiBOC glass was annealed at 1400 °C for 1, 3, 5 and 10 h and then it was HF etched in order to dissolve the SiO_2/B_2O_3 phase and to obtain a porous C-rich oxycarbide glass. The porous material was studied by N_2 absorption. The pore diameter of the porous C-rich SiBOC glass ranges between 2 and 5 nm and continuously increases with increasing annealing time. The pore volume also increases with the annealing time up to ≈1.0 cm^3/g which is close to the pore volume estimated from the chemical composition (1.04 cm^3/g) assuming complete dissolution of the silica-based phase.

Keywords: A. Precursors-organic; D. Carbon; D. SiC; D. SiO_2; Polymer-derived ceramics

1. Introduction

Silicon oxycarbide glasses, SiOC, belong to the family of polymer-derived ceramics (PDCs) and are obtained by pyrolysis of crosslinked hybrid siloxanes.[1,2] Historically, the interest for these new materials came from the possibility of improving the mechanical, thermal and chemical properties of silica via a partial substitution of bridging oxygen atoms with tetra-coordinated carbon atoms.[3] Following this idea, the presence of C atoms in the silica network as a separated graphitic phase was considered detrimental and therefore many studies have been devoted to control the composition of the SiOC network in order to preferentially insert C in the oxide structure via Si–C bonds and to decrease the percentage of sp^2 C atoms.[4–7] However, reducing the amount of free carbon in SiOCs is not an easy task and usually silicon oxycarbides do contain an extra carbon phase. More recently it has been recognized that the free carbon phase may not always be disadvantageous for the SiOC properties[8,9] as for example its high temperature stability.[10] As a result, studies devoted to the synthesis of C-rich SiOC glasses have been published.[11,12] The presence of graphene sheets in the SiOC nanostructure has been acknowledged by two models recently reported in the literature.[12,13] According to these models, the SiOC 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. The interface between the silica domains and the graphene sheets/SiC nanocrystals contains mixed silicon oxycarbide units.

It has been shown that these SiOC glasses can be used as precursors for porous C-based materials either by etching them with chlorine gas at high temperature[14] or with hydrofluoric acid solution.[15] In particular, the latter treatment with HF, preferentially dissolves the silica clusters and leaves behind a porous carbon-based material which contains Si and residual O, namely a porous, C-rich, silicon oxycarbide.[16] Interest for this novel form of C-rich SiOCs is driven by the recent discovery of new functional features such as increased H_2 and CH_4 gas storage[14] and very high reversible capacity for Li storage above 600 mAh/g, which make these materials candidate for substituting C anodes in Li ion batteries.[17]

In a previous study we have already shown that the pore size and pore volume of the porous carbon-rich materials, derived by HF etching, can be controlled by changing the maximum

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pyrolysis temperature of the parent SiOC glass.[18] In the present work we show that the nanostructural features of this porous material can also be controlled by varying the isothermal annealing time at the maximum temperature prior to HF etching. For this study, B-containing SiOCs, namely a SiBOC glass, has been chosen since it is known that B-containing silicon oxycarbides have a similar structure to SiOC glasses, with SiO_2–B_2O_3 clusters instead of the silica ones,[18] but they undergo a faster high temperature rearrangement compared to B-free SiOC samples,[16,18,19] thus allowing for reducing the experimental time.

2. Experimental

2.1. Sample preparation

SiBOC precursor gels were prepared from methyltriethoxysilane (MTES) and boric acid, following a procedure described earlier.[19] MTES was purchased from ABCR (Germany) and $B(OH)_3$ from Carlo Erba (Italy) and both reagents were used as received. The ratio between MTES and $B(OH)_3$ was chosen in order to have a molar ratio B/Si = 0.2. After drying the gel fragments were pyrolized in an alumina tubular furnace in flowing Ar (100 ml/min) at 10 °C/min up to 1400 °C and held at this temperature for 1, 3, 5 and 10 h. After the annealing step the furnace was shut down and let cool to room temperature. The etching process was performed on 0.5 g of 80–120 μm sieved oxycarbide powders using an HF (20 vol.% in H_2O) solution. The powders were stirred for 9 h at room temperature, then the solution was filtered and the powders were rinsed with distilled water and dried at 110 °C.

2.2. Chemical analysis

Chemical analysis of selected SiBOC glass samples before etching was performed by the Service Central d'Analyze du CNRS, Vernaison, France. Si, C, B and H were measured. O was estimated by the difference to 100%. Selected HF-etched SiBOC ceramics were analyzed for Si, C, B, O, H and F by the Analytisches Labor Pascher, Remagen-Bandorf, Germany.

2.3. X-ray diffraction study

XRD studies were conducted (Model D/Max-B, Rigaku Co., Tokyo, Japan) at 40 kV and 30 mA with CuKα radiation. The data collection was conducted from $2\theta = 10$–80° with a step of 0.05° and acquisition time 4 s.

2.4. N_2 adsorption measurements

The structure of the porous C-rich SiBOC glasses was characterized by N_2 adsorption analysis. The isotherms were collected at 77 K using an ASAP 2010 (Micromeritics, Gemini Model 2010, USA). The specific surface area, SSA, was determined using the BET equation with an accuracy of $\pm 10\ m^2/g$.[20] The total pore volume was calculated as, pore volume, $V = V_a \times D$, where V_a = volume adsorbed at P/P_0 0.99, D = density conversion factor (0.0015468 for nitrogen as adsorbate gas). The pore size distribution was obtained using the Barrette–Joynere–Halenda (BJH) method.[21] The micropore volume was determined by the Harkins–Jura method.

2.5. Transmission electron microscopy (TEM) investigations

Micro/nanostructural characterization of the HF etched and annealed samples was performed by TEM using a FEI CM20STEM instrument, operating at 200 keV (FEI, 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. It is worth noting that with the employed instrument (LaB_6 filament) it is difficult to simultaneously image SiC and turbostratic carbon. For SiC imaging, a higher defocus value of approximately −45 nm was set (Scherzer defocus), while imaging the carbon phase was typically done at a defocus setting of about −5 nm (Gauss defocus). Fig. 1 illustrates such a situation; the same region is shown at Scherzer versus Gauss defocus.

3. Results and discussion

Chemical analysis of selected SiBOC glass powders annealed at 1400 °C for 1 and 5 h are reported in Table 1. The B content is close to the nominal value. Chemical composition does not change after 10 h annealing at 1400 °C confirming that the SiBOC glasses are stable at high temperature and that the rearrangement of the glass network, which takes place above 1200 °C, occurs without decomposition and weight loss.[18,19,22]

The chemical composition of the HF etched SiBOC glasses is also reported in Table 1. The most remarkable feature emerging from the chemical analysis results on the HF etched samples is the progressive decrease of the oxygen content down to 31.0 and 11.1 wt.% after annealing for 1 and 10 h, respectively. These data confirm that hydrofluoric acid preferentially dissolves the oxide clusters of the SiBOC nanostructure and also show that increasing the annealing time results in a higher volume fraction of dissolved oxide phase. There is also a relative increase of the C content since C-clusters and C atoms bonded to Si atoms are not affected by the HF treatment.[16] Finally, after the HF attack, the porous C-based SiOC residue displays a higher H content and the presence of residual F. For the sample annealed for 10 h and then HF etched, the O/H atomic ratio is close to 1, suggesting that most of the O and H atoms are probably present as surface OH groups. On the other hand, residual fluorine could be either bonded to silicon, forming Si–F bonds or to carbon forming F-intercalated graphite.[23] In conclusion, the chemical analysis of the HF etched SiBOC glasses confirms the formation of C-rich silicon(boron)oxycarbide glasses. Moreover, increasing the annealing time increases the amount of oxide that can be dissolved by the HF attack.

The evolution of the XRD diffractograms recorded on the SiBOC glasses before and after HF etching is reported in Fig. 2.

Table 1
Chemical composition of selected SiBOC glasses after annealing and after HF treatment.

Annealing time at 1400 °C	Composition (wt.%)						Empirical formula
	Si	B	C	H	O	F	
1 h	41.0	3.2	11.8	<0.3	44.0	–	$SiB_{0,20}C_{0,67}O_{1,88}H_{<0,2}$
5 h	41.7	3.3	12.2	<0.3	42.8	–	$SiB_{0,21}C_{0,68}O_{1,80}H_{<0,2}$
10 h	42.0	3.2	12.2	<0.3	42.6	–	$SiB_{0,20}C_{0,68}O_{1,78}H_{<0,2}$
1 h-HF	30.9	2.17	41.9	0.7	31.0	1.5	$SiB_{0,18}C_{3,17}O_{1,10}H_{0,7}F_{0,07}$
10 h-HF	31.0	1.72	51.1	0.8	11.1	1.6	$SiB_{0,14}C_{3,86}O_{0,63}H_{0,7}F_{0,07}$

XRD patterns collected on SiBOC annealed at 1400 °C for different length of time before etching show the presence of the silica halo centered at about $2\theta \approx 22°$. Broad peaks at $2\theta \approx 35°$, 60° and 72° are due to the (1 1 1), (1 0 1) and (2 1 1) reflections of cubic β-SiC. The sp2 carbon (0 0 2) peak at $2\theta \approx 26.6°$, close to the main contribution of the silica glass is well hidden under it in the starting glass and becomes clearly exposed by the etching process. XRD patterns show a very slight evolution with increased annealing time: comparing the 1 and 10 h samples it is possible to see a slight increase of the intensity of the (1 1 1) reflection of SiC at $2\theta \approx 35°$ and a shoulder at $2\theta \approx 26.6°$ becomes slightly visible. The analysis of the line broadening, according to the Scherrer equation, has been performed on the (1 1 1) peak of SiC and allows to estimate the crystal size of 2.8 ± 0.2 nm after 1 h annealing and of 3.5 ± 0.2 nm after 10 h annealing at 1400 °C.

By increasing the annealing time, the etching of the oxide clusters of the SiBOC ceramic becomes more important (as was also shown by the chemical analysis after HF etching) and correspondingly the silica halo at $2\theta \approx 22°$ in the XRD diffractograms of the etched samples progressively decreases, accompanied by more intense reflections of the crystalline phases present in these glasses (SiC and graphitic carbon). The broadening line analysis performed on the (0 0 2) peak at $2\theta \approx 26.6°$ present in the XRD spectra of the etched samples reveals the nanometer-size of the C clusters in the direction orthogonal to the C sp2 basal plane

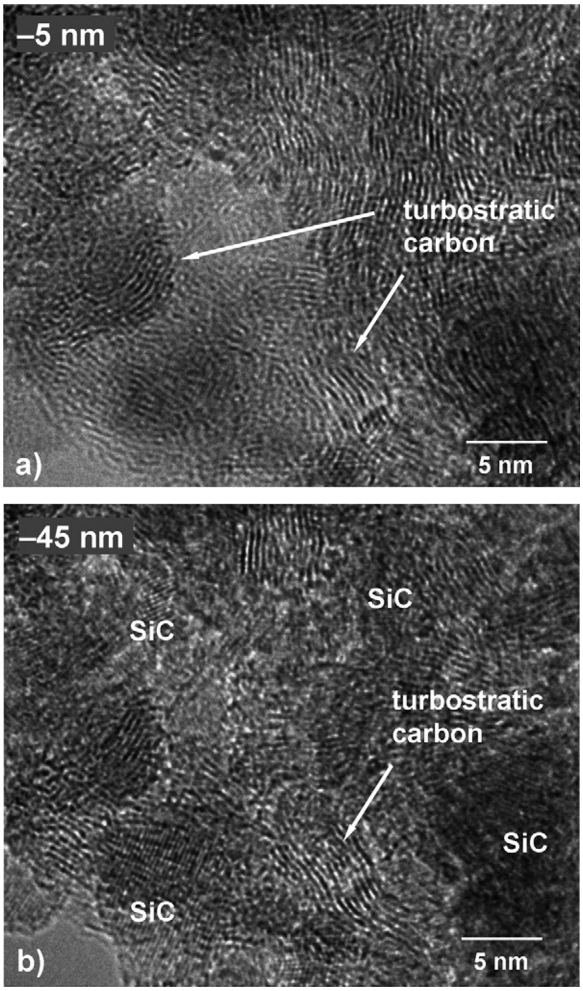

Fig. 1. HRTEM images of SiBCO annealed at 1400 °C for 10 h and subsequently HF etched. In (a) the carbon phase is clearly visible (Gauss defocus, −5 nm) while in (b) SiC precipitates become visible (Scherzer defocus, −45 nm), which are not clearly imaged in (a).

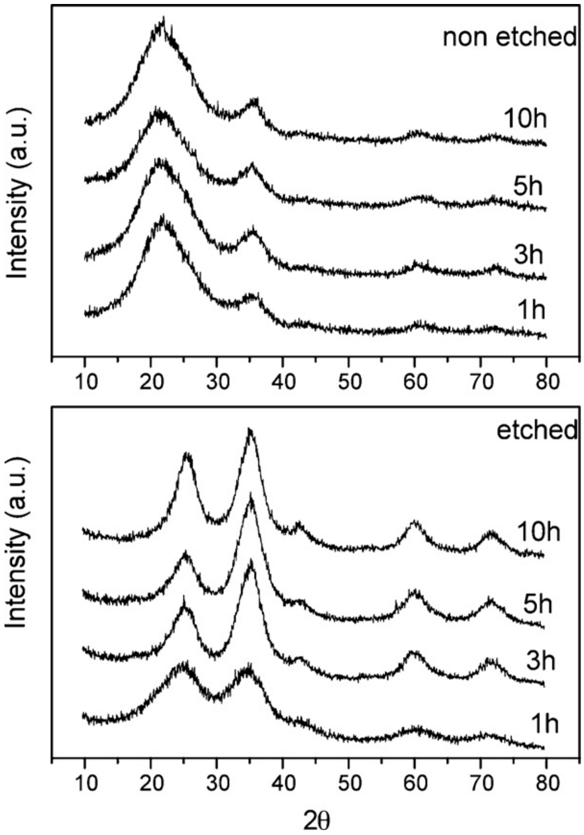

Fig. 2. XRD diffractograms recorded on the SiBOC ceramics annealed at 1400 °C for 1, 3, 5 and 10 h before and after HF etching.

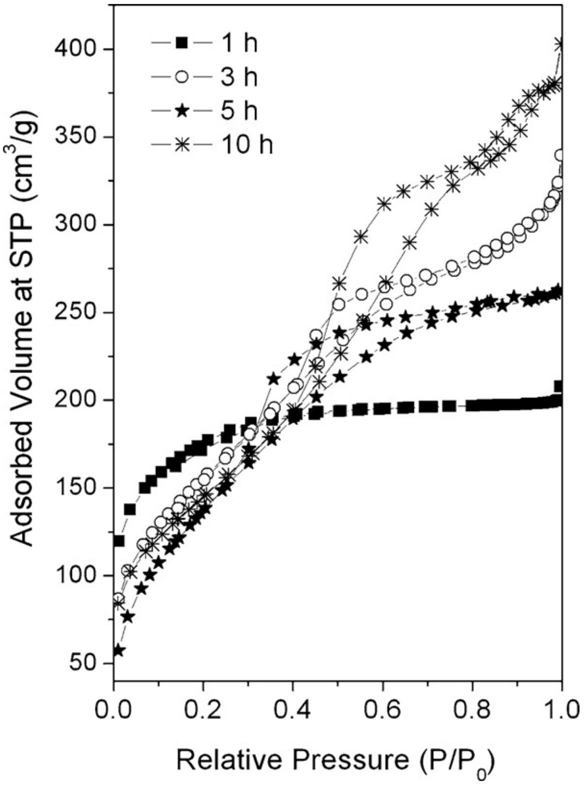

Fig. 3. Adsorption desorption isotherms of the HF etched SiBOC glass as a function of the annealing time at 1400 °C.

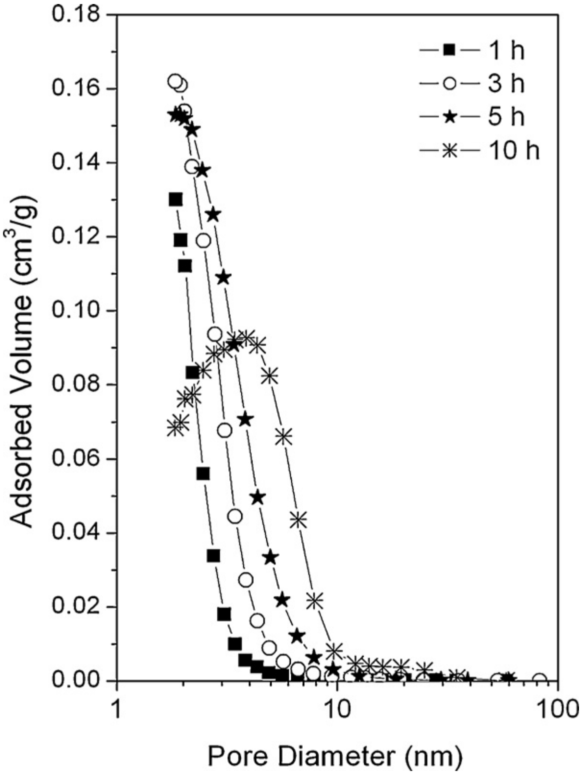

Fig. 4. Pore size distribution of the HF etched SiBOC glass as a function of the annealing time at 1400 °C.

being 2.9 ± 0.2 nm after 1 h and 5.1 ± 0.2 nm after 10 h annealing. Accordingly, the XRD study proves that the isothermal annealing induces a growth of both the cubic silicon carbide and the graphitic carbon nanocrystals, in agreement with previously published data.[18,19]

The adsorption–desorption isotherms collected on the porous oxycarbide glasses obtained after HF etching are shown in Fig. 3 and can be classified as Type IV according to the IUPAC nomenclature.

The corresponding characteristic features are reported in Table 2.

At higher pressure samples annealed for more than 1 h clearly show a hysteresis loop, which is caused by the capillary condensation in the mesopores. The sample with the longest annealing time (10 h) even shows a second hysteresis loop close to the saturation pressure. At lower pressures ($P/P_o < 0.04$) 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 HF-etched SiOC samples is shown in Fig. 4.

The data reported in Table 2 and Fig. 4 show clearly that the pore volume and pore size of the porous C-rich SiBOCs continuously increases with the annealing time of the parent SiBOC glass. After 10 h 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 at <2 nm. The pore size measured for 1 h annealing time, between 2 and 4 nm, agrees quite well with the mesopore size distribution reported by Vakifahmetoglu et al.[14] obtained by chlorination a polymer-derived SiOC pyrolyzed at lower temperature (1200 °C) for 2 h. In their work, a mesopore size ranging from 2 and 4 nm has been found for the SiOC glass with similar Si, O and C content as the SiBOC glass studied here. They explained the mesopore formation by the removal of Si and O from the silicon oxycarbide network.

The evolution of the meso, micro and total pore volume with the annealing time is reported in Fig. 5.

The volume of the micropores does not show a strong dependence on time while the meso and therefore the total pore volume

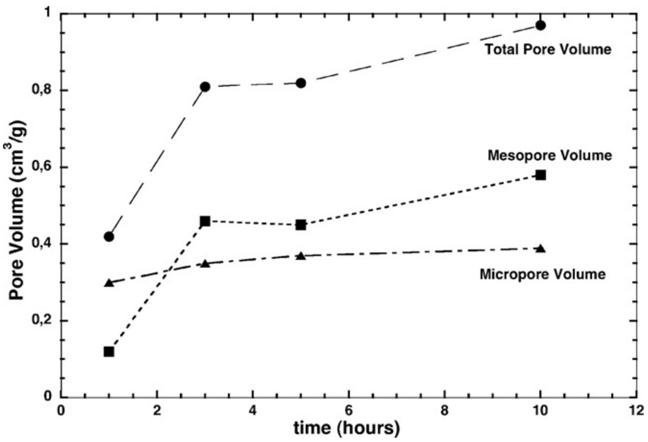

Fig. 5. Meso, micro and total pore volume of the HF etched SiBOC glass as a function of the annealing time at 1400 °C.

Table 2
Specific surface area, SSA, meso, micro and total pore volume of the porous C-rich SiBOC glasses obtained from the N_2 adsorption characterization.

Annealing time at 1400 °C	SSA (m^2/g)	Mesoporous volume (cm^3/g)	Microporous volume (cm^3/g)	Total pore volume (cm^3/g)
1 h	567	0.12	0.30	0.42
3 h	570	0.46	0.35	0.81
5 h	533	0.45	0.37	0.82
10 h	524	0.58	0.39	0.97

is more affected by the length of the isothermal treatment. In spite of the fact that pore volume increases with annealing time the SSA slightly decreases (Table 2). This apparent discrepancy could be explained assuming that the pore size increases more than the pore volume therefore leading to a decrease of SSA. The total pore volume almost doubled from 1 to 5 h (from 0.42 cm^3/g to 0.82 cm^3/g) and reaches a maximum value of 0.97 cm^3/g after 10 h. The evolution of the total porosity, as recorded by BET analysis, is consistent with the TEM observations. Figs. 6 and 7 reveal the change in nanostructure upon annealing for 1 and 10 h at 1400 °C.

TEM images clearly show that the pore structure changes with annealing time; i.e. the pore size considerably increases. In addition, it is worth noting that the carbon phase also undergoes alteration. While upon annealing for 1 h predominantly turbostratic carbon was observed, the maximum heat treatment for 10 h at 1400 °C resulted in the formation of graphitic carbon (compare Figs. 6(a) and 7(a)).

This nanostructural evolution has its origin in the phase separation process, which occurs in the silicon oxycarbide glasses at higher temperatures ($2SiOC \Rightarrow SiO_2 + SiC + C$). It is known that at low temperature, i.e. <1200 °C, the SiOC glass network contains the maximum amount of mixed silicon oxycarbide units, SiC_xO_{4-x}, $1 \leq x \leq 3$ and that by increasing the annealing temperature and/or time, the network undergoes a phase separation process with a depletion of the mixed units, accompanied by an increase of the SiC_4 and SiO_4 units and the ordering of the free carbon phase.[4–7,18,19] The progressive increase of SiC_4 and SiO_4 units results in a progressive growth of the SiC nanocrystals, as it was also observed by the XRD analysis, and SiO_2 nanoclusters. For the present case in which a SiBOC glass is studied, the oxide clusters are better described as a borosilicate glass.[18] The SiO_4 and BO_3 units, which are present in the borosilicate nanodomains, can be leached out by HF thus forming the porous C-rich SiBOC glass. For the sake of clarity, we need to remind that only the silicon and boron atoms in SiO_4 and BO_3 units can be leached out while silicon and boron present in mixed oxycarbide units with at least one Si–C or B–C bond are still stable. Indeed, Si–C and B–C bonds cannot be cleaved by HF attack and therefore they act as a permanent bridge to the C-rich phase.[8,15] As a consequence, if by increasing the temperature or, as in this case, extending the annealing time, the fraction of Si and B atoms present in the borosilicate nanodomains increases, the pore volume and the pore size of the resulting porous oxycarbide glass also increases.

The evolution of the total pore volume with time suggests that the amount of porosity reaches a plateau after 10 h. Indeed, the total pore volume measured after the longest annealing time (0.97 cm^3/g 10 h), is very close to the porosity value estimated by assuming that the HF treatment completely removes the oxide phase present in the SiBOC glass (estimated porosity = 1.04 cm^3/g, see Appendix A for the corresponding calculation). The agreement between the measured and estimated porosity is quite remarkable in view of the various sources of error, which can affect the calculation such as: (i) the precision of chemical analysis and (ii) the estimated density of the borosil-

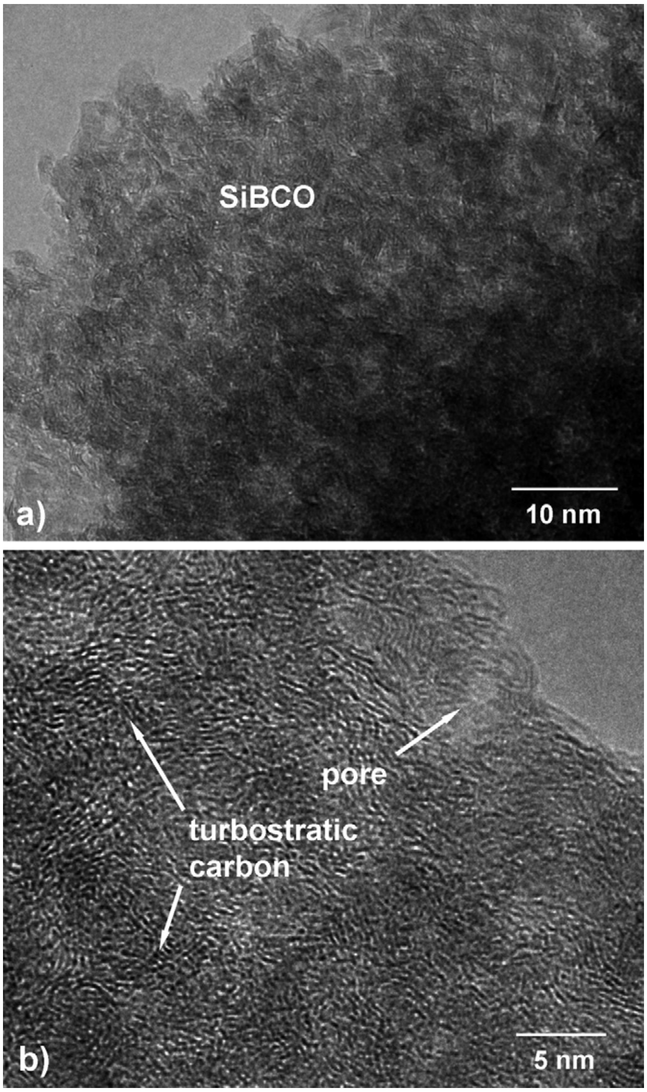

Fig. 6. HRTEM images of SiBCO annealed at 1400 °C for 1 h (subsequently HF etched). In (a), an overview of the nanostructure is given, while (b) depicts such an area at higher magnification. The pore size in this material is approximately ≤2 nm.

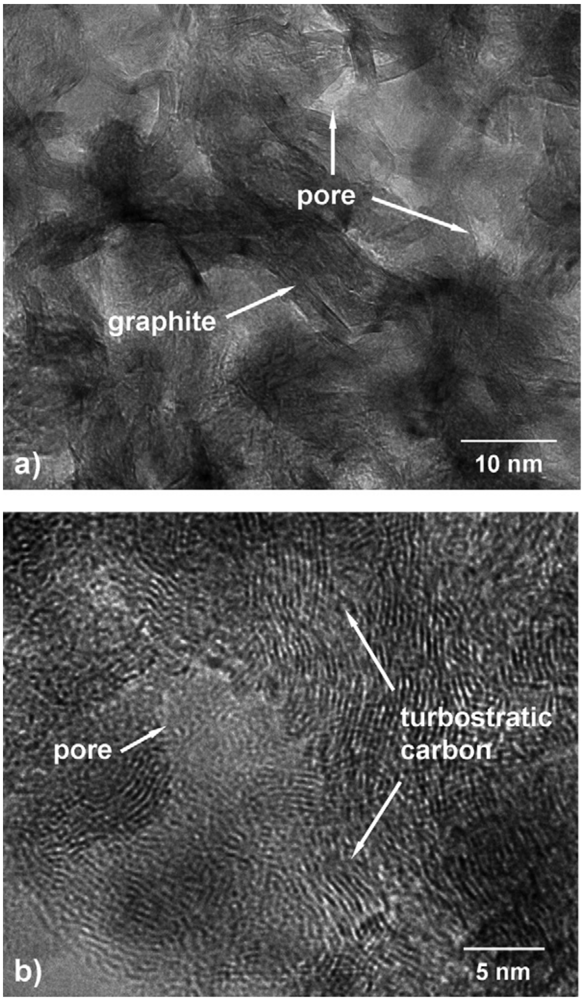

Fig. 7. HRTEM images of SiBCO annealed at 1400 °C for 10 h (HF etched). In (a), an overview of the nanostructure is given, while (b) shows the material at higher magnification. The pore diameter in this material is approximately ≤5 nm.

icate phase. This result seems to suggest that after 10 h annealing at 1400 °C the phase separation process is complete and the HF attack is able to dissolve the borosilicate phase up to a large extent. Indeed, the residual oxygen, which has been revealed by the chemical analysis in the HF etched sample annealed for 10 h, is probably confined to the pore surfaces as OH groups. Another interesting information that emerges from the agreement between the estimated and measured porosity is that the C-rich phase (containing also SiC nanocrystals) has to form a continuous network. Otherwise the dissolution of the oxide phase would not lead to the formation of a porous nanostructure with the expected porosity value.

4. Conclusion

The effect of annealing time on the nanostructural development of porous C-rich silicon(boron)oxycarbide material derived from a SiBOC glass was investigated. The study was performed by isothermal annealing at 1400 °C for holding times of 1, 3, 5 and 10 h. Upon thermal treatment the SiBOC glass was HF etched in order to dissolve the silica-based phase and to produce a porous oxycarbide glass. Maximum values of specific surface area and total pore volume of 570 m^2/g and 0.97 cm^3/g, respectively, have been obtained. The N_2 adsorption analysis showed that the pore volume continuously increases with annealing time, reaching the maximum of 0.97 cm^3/g, which is very close to the estimated values considering the complete removal of the oxide phase from the C-based network. The pore size of the synthesized porous SiBOC ranges between 2 and 5 nm and increases with the annealing. Potential applications of such nanoporous SiBOC materials are seen as hydrogen storage materials and/or as anode material in Li-ion batteries.

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Appendix A.

The maximum pore volume of the porous SiBOC can be estimated from the chemical analysis data as follows:

- the composition of the SiBOC glass, $Si_1B_xC_yO_z$ is re-written considering that:
  1. all the boron is forming B_2O_3, then: moles of $B_2O_3 = x/2$
  2. the remaining oxygen forms SiO_2, then: moles of $SiO_2 = (z - 3x/2)/2$
  3. the remaining silicon forms SiC, then: moles of $SiC = 1 -$ moles of $SiO_2 = 1 - ((z - 3x/2)/2)$
  4. The remaining carbon is present as free C, then: moles of $C = z -$ moles of $SiC = z - (1 - ((z - 3x/2)/2))$.

Accordingly, the composition of the SiBOC glasses measured at 1400 °C after 10 h can be re-written as:

- $SiB_{0.20}C_{0.68}O_{1.78} = 0.74SiO_2\ \ 0.10B_2O_3\ \ 0.26SiC\ \ 0.42C_{free}$ multiplying by the molecular weight results in:
- 44.4 g SiO_2 6.90 g B_2O_3 10.4 g SiC 5.04 g C_{free}

Assuming that all the B_2O_3 is present in a borosilicate glass (overestimation) with a density of 2.2 g/cm^3, and assuming that the borosilicate glass will be etched completely we can estimate the pore volume as:

- Total pore volume $= \frac{44.4+6.90}{2.2} = 23.32\ cm^3$

Finally we can convert the total pore volume in total pore volume per gram by dividing by the weight of the carbon residue:

- $\frac{\text{Total pore volume}}{\text{gram}} = \frac{23.32}{10.4+5.04} = 1.04\ cm^3/g$

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