

Structural Characterization and High-Temperature Behavior of Silicon Oxycarbide Glasses Prepared from Sol-Gel Precursors Containing Si-H Bonds

Gian Domenico Sorarù,* Gennaro D'Andrea, and Renzo Camprostrini

Dipartimento di Ingegneria dei Materiali, Università di Trento, 38100 Trento, Italy

Florence Babonneau

Chimie de la Matière Condensée, Université Pierre et Marie Curie, CNRS, 75005 Paris, France

Gino Mariotto

Dipartimento di Fisica, Università di Trento, 38050 Povo, Trento, Italy

Silicon oxycarbide glasses have been synthesized by inert atmosphere pyrolysis at 1000°C of gel precursors obtained by cohydrolysis of triethoxysilane, HSi(OEt)₃, and methyl-diethoxysilane, HMeSi(OEt)₂. The oxycarbide structures have been carefully characterized by means of different techniques such as ²⁹Si magic angle spinning nuclear magnetic resonance (MAS-NMR) and Raman spectroscopies, X-ray diffraction (XRD), and chemical analysis. Experimental results clearly indicate that, depending on the composition of the starting gels, the resulting oxycarbide glass either is formed by a pure oxycarbide phase or contains an extra carbon or silicon phase. By increasing the temperature up to 1500°C, the oxycarbide glasses display compositional and weight stability; however, the amorphous network undergoes structural rearrangements that lead to the precipitation of nano-sized β-SiC crystallites into amorphous silica. Crystallization of metallic silicon is also clearly observed at 1500°C for the samples in which the presence of Si-Si bonds was postulated at 1000°C.

I. Introduction

SILICON OXYCARBIDE glasses are a new class of amorphous solids derived from the structure of silica glass in which part of the divalent oxygen atoms have been replaced with tetracoordinated carbon atoms.¹ The ideal composition of a silicon oxycarbide phase consisting only of Si-O and Si-C bonds, with no Si-Si, C-O, and C-C bonds, is SiC_xO_{2(1-x)}, in which one tetravalent carbon atom substitutes for two divalent oxygen atoms. This substitution leads to the presence, in the amorphous network, of carbidic carbon units, [C(Si)₄], which strengthen the structure by increasing its bond density. Thus, all of the physical and chemical properties directly related to the structure of the amorphous network, such as the elastic modulus, hardness, density, viscosity, glass transition temperature, and chemical durability, are expected to increase with the amount of incorporated carbon. Indeed, literature data on the characterization of these novel materials indicate superior properties for the C-containing glasses compared to the parent fully oxide systems.¹⁻³ Moreover, preliminary results obtained in our laboratory³ and also reported in the literature⁴⁻⁸ indicate the possibility

of crystallizing nano-sized SiC from the oxycarbide glass, thus giving the opportunity of processing *in situ* silicon carbide reinforced silica nanocomposites.

Silicon oxycarbide glasses can be produced by pyrolysis in an inert atmosphere of polysiloxanes.²⁻²¹ These precursors can be synthesized via the sol-gel route starting from organically modified silicon alkoxides, R'_x-Si(OR)_{4-x}. R' is usually a methyl group.^{4-7,9-11,13,16,18,21} However, other organic groups containing more C atoms were introduced in silica gels such as ethyl, propyl, phenyl, vinyl, or allyl:^{4-5,11} in the case of alkyl chains, carbon is lost during the pyrolysis by β-elimination, and thus the final C content is similar to that obtained with methyl groups. In contrast, with phenyl or unsaturated side chains, the residual C content is much higher and leads to the formation of an important free carbon phase. Methyl-substituted silica gels thus appear as the most suitable precursors for silicon oxycarbide glasses.

²⁹Si magic angle spinning nuclear magnetic resonance (MAS-NMR) experiments clearly indicated that part of the Si-C bonds present in the precursor gel are retained in the pyrolyzed product, thus leading to the expected oxycarbide structure.^{2,8,10-12} However, even for the methyl-substituted systems, Raman spectroscopy,^{13,19} transmission electron spectroscopy (TEM),² quantitative MAS-NMR analysis,^{16,21} and also the black color of the oxycarbide samples show that, in the gel-derived oxycarbide glasses, part of the carbon atoms are present in a second phase as free carbon. Therefore, the system must be described as a composite material formed by a silicon oxycarbide matrix of the general formula SiC_xO_{2(1-x)} and a dispersed free carbon phase.^{5,11} The problem of controlling the composition of the resulting oxycarbide phase, i.e., the *x* value of substituted C, and the amount of the free carbon phase, has been recently addressed in the literature by one of the present authors for the methyl-modified silica gels.²² This study suggests that, as a first approximation, the amount of carbidic carbon in the oxycarbide structure, (C/Si)_{oxy}, is related to the oxygen content of the precursor gel, (O/Si)_{gel}, via the relationship

$$(C/Si)_{oxy} = \{4 - [(O/Si)_{gel} \times 2]\}/4 \quad (1)$$

It is based on the assumption that the number of Si-O bonds remains constant during the transformation process from the gel to the oxycarbide structure. This assumption was established based on available published data on the compositions of the starting gels and the corresponding pyrolyzed products.²² In the same study, it was suggested that, when the C content of the precursor gel is higher than the amount of carbon required to form the oxycarbide phase according to Eq. (1), a free carbon

C. Pantano—contributing editor

Manuscript No. 193715. Received March 29, 1994; approved August 29, 1994. Supported by NATO under Contract No. CRG 931453 and by MURST 40%. *Member, American Ceramic Society.

phase can form. For example, fully condensed silica gels obtained from tetraethoxysilane, $\text{Si}(\text{OEt})_4$ (TEOS), and dimethyldiethoxysilane, $\text{Me}_2\text{Si}(\text{OEt})_2$ (DMDES), copolymers in a 1/1 ratio with $(\text{O}/\text{Si})_{\text{gel}} = 1.5$ should lead to the following oxycarbide phase: $\text{SiC}_{0.25}\text{O}_{1.5}$. Moreover, the carbon content of the gel is $(\text{C}/\text{Si})_{\text{gel}} = 1 \gg (\text{C}/\text{Si})_{\text{oxy}} = 0.25$ and therefore a free carbon phase could be present in the pyrolyzed samples. Experimental results are in good agreement with this model; the C/Si ratio in the 1000°C sample is 0.56. So almost 50% of the initial C was eliminated through gaseous products (methane, but also silanes); the residual C was found in the oxycarbide phase [$(\text{C}/\text{Si})_{\text{oxy}} \approx 0.15$] and also in a free carbon phase.²¹

Modified silica gels obtained from cohydrolysis of triethoxysilane, $\text{HSi}(\text{OEt})_3$ (TREOS), and methyldiethoxysilane, $\text{HMeSi}(\text{OEt})_2$ (MDES), are attractive precursors for oxycarbide glasses due to the possibility of changing the oxygen and carbon content in the gel by varying the relative amount of the two alkoxides. For these gels, the amount of carbon is related to the amount of oxygen according to the solid line of Fig. 1 and it ranges from a value of 0 for 100% TREOS composition up to 1 for the 100% MDES sample. In the same figure, the dotted line shows the relationship between the C and O contents in the stoichiometric oxycarbide phase. The two lines cross each other for a value of $\text{O}/\text{Si} = 1.33$, corresponding to a gel composition of 66.7 TREOS·33.3 MDES (mol%). In this case, the carbon content of the gel matches the amount of carbon of the corresponding oxycarbide phase and therefore the tendency for the system to form a C_{free} phase should be low. Following the same idea, the formation of a free carbon phase should be favored for gel compositions with $\text{O}/\text{Si} < 1.33$, i.e., TREOS content lower than 66.7%, whereas when $\text{O}/\text{Si} > 1.33$, i.e., for TREOS content higher than 66.7%, the pyrolysis process should lead to the formation of an oxycarbide phase with a carbon deficiency, thus leading to the presence of Si-Si bonds. Indeed, it has already been proved experimentally by quantitative ²⁹Si MAS-NMR analysis that gels with the 66.7 TREOS·33.3 MDES composition pyrolyzed at 1000°C lead to an almost pure silicon oxycarbide glass while a C_{free} phase was observed in the black glass derived from the 50 TREOS·50 MDES (mol%) composition, in agreement with the previous analysis.¹⁸

The present study focuses on the high-temperature behavior up to 1500°C of the oxycarbide glasses produced from TREOS/MDES copolymers pyrolyzed at 1000°C. Compositions of the starting gels have been chosen in order to get, after the pyrolysis process, the two different structures as previously discussed, i.e., the almost pure oxycarbide phase (66.7 TREOS·33.3 MDES) and the system with a C_{free} phase (50 TREOS·50 MDES). An additional gel with TREOS content higher than

66.7% has been studied to verify the hypothesis of the formation, when $(\text{O}/\text{Si})_{\text{gel}} > 1.33$, of an oxycarbide network with not only Si-O and Si-C but also Si-Si bonds.

II. Experimental Procedure

Three gel compositions, labeled A, B, and C, have been studied with a TREOS content = 50, 66.7, and 90.9 mol%, respectively (Fig. 1). The chosen compositions have a TREOS/MDES ratio of 1, 2, and 10, respectively. Weighted amounts of the two alkoxides (K&K, New York) were mixed in ethanol ($\text{EtOH}/\text{Si} = 2$) and hydrolyzed with distilled water ($\text{H}_2\text{O}/\text{OR} = 1$; $\text{pH} \approx 6$). The solution was stirred for 15 min and then poured into open test tubes. Gelation times range from a few hours for the TREOS-rich composition up to a few days for the MDES-rich gel. Transparent, monolithic gels were obtained after a drying process of 1 week at room temperature and 24 h at 80°C. Weight losses and thermal effects associated with the pyrolysis process were monitored on powdered samples by performing TG/DTA analysis in flowing argon on Netzsch equipment up to 1550°C with a heating rate of 5°C/min.

Black glasses were produced from the gels by a pyrolysis process at 1000°C in flowing Ar (100 cm³/min). Samples were placed in a furnace equipped with a silica tube and heated 5°C/min with a holding time of 1 h at the maximum temperature. The oxycarbide samples were then fired in a graphite furnace at various temperatures up to 1500°C using the same heating schedule and atmosphere. Selected samples were analyzed for Si, C, and H contents by the Service d'Analyse Elementaire du CNRS, France. Oxygen was estimated by difference.

²⁹Si MAS-NMR spectra were collected with a MSL 400 Bruker spectrometer (79.5 MHz). The powdered samples were put in 7-mm zirconia rotors and spun at 4 or 5 kHz. The spectra were recorded using a spectral width of 50 000 Hz with pulse width of 2.5 μs ($\Theta \approx 30^\circ$) and relaxation delays of 60 s. Because of long ²⁹Si relaxation times, quantitative analysis of the NMR data is always delicate. However, the parameters used in this study should give a general trend in the evolution of the various Si sites;²⁰ 1000 to 1500 transients were recorded and a line-broadening procedure (50 Hz) was applied before Fourier transform.

A Rigaku diffractometer operating at 40 kV and 30 mA, equipped with a graphite curved crystal monochromator in the diffracted beam, was used to record the XRD spectra of powdered samples fired at various temperatures. A JEOL 100CX II instrument was used to perform TEM investigations on fine powders dispersed on a copper grid.

Room-temperature Raman spectra were recorded, in a 90° scattering geometry, on monolithic pyrolyzed samples by exciting the samples in air with an Ar⁺ ion laser operating at 488.0 nm. The scattered radiation was dispersed with a double monochromator (Jobin-Yvon, Ramanor HG2-S), equipped with holographic gratings (1800 line/mm), and detected with a cooled photomultiplier interfaced with a standard photon counting system. Well reproducible Raman spectra, of remarkable intensity and of quite good signal-to-noise ratio, were collected with a single scan.

III. Experimental Results

(1) Characterization of the Gels

Chemical analysis of the gel samples is reported in Table I. The C/Si ratio for the A and B compositions (0.51 and 0.35, respectively) are very close to the expected values (0.5 and 0.33, respectively) calculated assuming that the condensation reactions are complete, with no residual Si-OH or Si-OEt groups in the gels. These results suggest that all the Si-CH₃ moieties of the MDES precursor survive the gelation process and that the gel networks are fully condensed. For the 10/1 composition (sample C), the experimental C/Si ratio (0.16) is

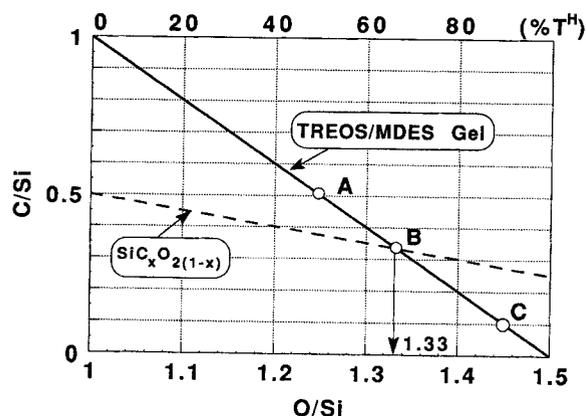


Fig. 1. C/Si vs O/Si for gel samples obtained from cohydrolysis of TREOS and MDES (solid line) and for the stoichiometric oxycarbide phase (dotted line). The compositions of the studied gels (A, B, and C) are also reported.

Table I. Chemical Analysis of the Gels and Their Ceramic Yields

Sample	Composition (wt%)				Empirical formula	C/Si*	TG (yield %)
	Si	C	O	H			
A	47.22	10.38	38.15	4.25	SiC _{0.51} O _{1.42} H _{2.53}	0.5	84
B	48.90	7.26	40.34	3.50	SiC _{0.35} O _{1.44} H _{2.01}	0.33	90
C	49.61	3.295	44.56	2.53	SiC _{0.16} O _{1.58} H _{1.43}	0.09	96

*Theoretical value calculated from the TREOS/MDES ratio assuming fully condensed gels and complete retention in the gel structure of the Si-CH₃ groups of MDES.

higher compared to the theoretical one (0.09). This difference, however, can be easily accounted for by the presence in the gel of only 1 mol% of nonhydrolyzed Si-OEt groups.

²⁹Si MAS-NMR analysis shows unequivocally the presence of the Si-H and Si-C bonds in the gel network (Fig. 2). NMR spectra display two main peaks at -84 ppm (HSiO₃ units) and at -34 ppm (HSiCO₂ units) and two less intense peaks at -110 ppm (SiO₄ units) and at -64 ppm (SiCO₃ units). All of the detected NMR peaks can be assigned to fully condensed silicon units and no evidence was found for terminal groups such as Si-OH or Si-OEt. The experimental spectra were simulated to get a quantitative estimation of the various silicon sites present in the gels (Table II), which suggests that the Si-H bonds are retained to a large extent in the gels and only a few percent of them are hydrolyzed, leading either to SiO₄ or SiCO₃ units. The quantitative analysis of the ²⁹Si MAS-NMR spectra also allows one to estimate the amount of carbon directly bonded to silicon atoms (Table II). These values, for all three gels, are in excellent agreement with the theoretical ones and confirm the stability of the Si-C bonds of MDES toward the hydrolysis reaction. Therefore, the three gels can be described as formed by a fully condensed silica network containing almost all of the Si-H and Si-CH₃ groups introduced with the TREOS and MDES precursors, without appreciable amounts of unreacted Si-OEt or uncondensed Si-OH moieties.

The three gel samples display similar thermogravimetric behavior with only one main weight loss between 400° and 500°C and no weight loss above 1000°C up to 1500°C.

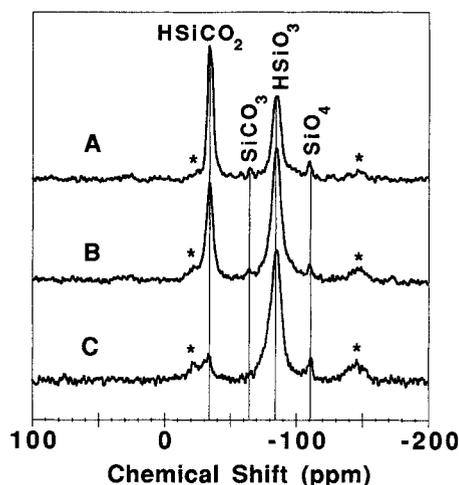


Fig. 2. ²⁹Si MAS-NMR spectra of the A, B, and C gels; (*) spinning sidebands.

The ceramic yield at 1000°C is very high, always over 84% (Table I). A detailed study of the conversion process performed mainly by using the ²⁹Si MAS-NMR technique will be reported elsewhere.²³

(2) Characterization of the Black Glasses

Pyrolysis of the gels at 1000°C leads to X-ray amorphous oxycarbide glasses. Chemical analyses performed on the black glasses pyrolyzed at 1000°C are reported in Table III. The C/Si ratio does not change during the pyrolysis process, which is the same, within the accuracy of the experimental method, for the gel samples and for the corresponding ceramic chars. Chemical analysis can help in understanding the structure of the pyrolyzed gels. Indeed, assuming the general formula SiC_xO_{2(1-x)} for the oxycarbide phase, from the experimental O/Si value, it is possible to estimate the C/Si value of the oxycarbide structure. Thus, by comparing these results with the total amount of carbon derived from chemical analysis, it is possible to estimate the amount of free carbon, if any. When the total carbon content is not enough to saturate all of the free valences on silicon atom, then some Si-Si bonds could form. The stoichiometry of the oxycarbide phase and the excess C or Si, if any, is reported in Table III. For gel A, ≈40 mol% of the total carbon is present in a free carbon phase while, for gel B, an almost pure oxycarbide phase has been obtained. As for the ceramic char derived from gel C, this analysis suggests the formation of Si-Si bonds. These results, for the three systems, are in good agreement with what was expected.

NMR spectra recorded on these samples are reported in Fig. 3. Compositions A and B, with a higher carbon content, display similar spectra with three broad NMR peaks in the chemical shift ranges 0 to -40 ppm, -50 to -80 ppm, and -90 to -120 ppm, associated with all of the possible mixed silicon oxycarbide sites SiC_xO_{4-x} with 0 ≤ x ≤ 4, i.e., SiO₄ at ≈ -108 ppm, SiCO₃ at ≈ -70 ppm, SiC₂O₂ at ≈ -35 ppm, SiC₄ at ≈ -16 ppm, and SiC₃O at ≈ -5 ppm. The NMR spectrum of the C sample is dominated by the SiO₄ component with a smaller resonance peak assigned to the SiCO₃ site and also a very small and broad peak in the chemical shift range (0 to -40 ppm) typical of Si atoms in SiC₄, SiC₃O, and SiC₂O₂ units. These results show that the pyrolytic conversion of the studied gels actually leads to the formation of an amorphous oxycarbide structure built by a random array of silicon oxycarbide units SiC_xO_{4-x} with 0 ≤ x ≤ 4. This was already seen by various groups,¹⁰⁻¹² but what is important is to extract the C content of the oxycarbide phase. A quantitative description of the amorphous oxycarbide networks in terms of the various silicon sites, SiO₄, SiCO₃, SiC₂O₂, SiC₃O, and SiC₄, can be determined by simulating the experimental ²⁹Si MAS-NMR spectra with the individual components. The results are reported in Table IV.

Table II. ²⁹Si MAS-NMR Characterization of the Gels

Sample	SiO ₄		HSiO ₃		SiCO ₃		HSiCO ₂		C/Si*	H/Si*
	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%		
A	-109.9	4	-83.7	46	-64.5	2	-33.7	48	0.50	2.43
B	-110.0	2	-84.8	65	-64.4	1	-34.3	32	0.32	1.93
C	-111.7	3	-85.6	88			-33.9	9	0.09	1.24

*Values calculated from ²⁹Si MAS-NMR analysis assuming a fully condensed network.

Table III. Chemical Analysis of Black Glasses Fired at 1000°C for 1 h*

Sample	Composition (wt%)			Empirical formula	Oxycarbide stoichiometry [†]
	Si	C	O		
A	49.17	9.72	40.81	SiC _{0.46} O _{1.46}	SiC _{0.27} O _{1.46} + 0.19C
B	51.78	7.03	40.88	SiC _{0.32} O _{1.39}	SiC _{0.30} O _{1.39} + 0.02C
C	49.67	2.45	47.57	SiC _{0.12} O _{1.68}	SiC _{0.12} O _{1.75} + 0.04Si

*The hydrogen content was found to be lower than 0.30 wt% for all of the samples and is not reported here. [†]The reported oxycarbide stoichiometry and the amount of free carbon or silicon is calculated on the basis of the experimental O/Si ratio as explained in the text.

The corresponding oxycarbide stoichiometries have been calculated assuming all C atoms in carbidic carbon units [C(Si)₄].

For sample A, the composition of the oxycarbide phase established by NMR, SiC_{0.30}O_{1.4}, is in very good agreement with that determined by chemical analysis (Table III), thus suggesting strongly the presence of a free carbon phase that should contain, according to the NMR analysis, ≈35 mol% of the total C content.

For sample B (SiC_{0.37}O_{1.25}), the agreement between NMR (C/Si ≈ 0.37) and chemical analysis (C/Si ≈ 0.30) results is not so good. However, these two values can be considered as equivalent to each other within the range of experimental error, especially considering that the C/Si ratio from NMR should be equal to or less than the total amount of C derived from chemical analysis, i.e., C/Si ≤ 0.32. Indeed, by taking into account the rather high level of noise in the NMR spectra, the accuracy of the NMR quantitative analysis cannot be high and the results should be examined more to understand the general trend in the compositional evolution rather than to get very precise compositional information. Thus the ceramic char from gel B could be described as an almost pure oxycarbide phase with no or very low amount of free carbon.

For sample C, chemical analysis results suggest the presence of Si-Si bonds, probably in mixed silicon oxycarbide units such as Si(Si_xC_yO_z) with x + y + z = 4. Unfortunately, the chemical shifts for these mixed silicon units are known for very few cases, such as Si(SiCO₂) (δ = -22 ppm), Si(SiC₂O) (δ ≈ 0 ppm), and have been usually reported for siloxane compounds in which the carbon environments are C(H₃Si) and not C(Si)₄.¹⁷

The only reported value that could be directly used for the oxycarbide systems is that of metallic silicon, i.e., Si(Si)₄ (δ = -80 ppm).²⁴ The NMR spectrum of sample C can be satisfactorily explained in terms of only Si-O and Si-C bonds. ²⁹Si NMR peaks at ≈ -70 and ≈ -110 ppm can be assigned respectively to SiCO₃ and SiO₄ units. However, a careful observation of the ²⁹Si MAS-NMR peak at ≈ -70 ppm (Fig. 4) suggests that a component at ≈ -80 ppm, assigned to Si(Si)₄ units, could be present. The simulation of this spectrum was done including this component, and gave the following stoichiometry: SiC_{0.12}O_{1.77} + 0.06Si, in good agreement with the composition extracted from chemical analysis (Table III), suggesting that ≈6 mol% of the silicon atoms could be present in an environment similar to that found in metallic silicon. Indeed the presence of Si-Si bonds will be strongly confirmed by the XRD study discussed later in this paper.

Thus, both NMR and chemical analysis studies strongly suggest that the structure of the ceramic chars derived from gels A, B, and C depend on the composition of the starting gels. Sample B can be described as an almost pure oxycarbide phase. Sample A contains an additional free carbon phase, while sample C could present an extra metallic silicon phase. However, in this last sample, the Si-Si bonds could be present within the oxycarbide network.

(3) High-Temperature Evolution of Sample A

The black glass obtained after firing gel A at 1000°C has been fired at 1200°, 1400°, and 1500°C with 1 h of holding time at the maximum temperature in order to study its high-temperature stability.

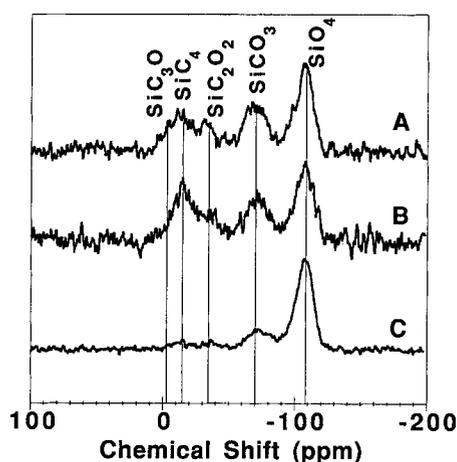


Fig. 3. ²⁹Si MAS-NMR spectra of the A, B, and C gels pyrolyzed at 1000°C for 1 h.

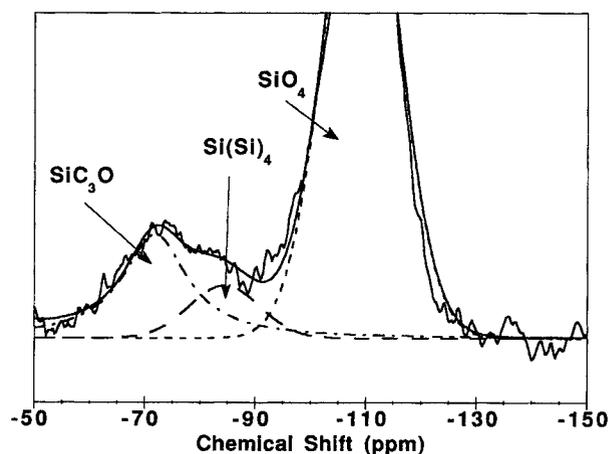


Fig. 4. Enlargement of the ²⁹Si MAS-NMR spectrum of gel C pyrolyzed at 1000°C for 1 h. The various components used for the simulation of the spectrum are also shown.

Table IV. ²⁹Si MAS-NMR Characterization of the Oxycarbide Glasses Fired at 1000°C for 1 h

Sample	SiO ₄		SiCO ₃		SiC ₂ O ₂		SiC ₃ O		SiC ₄		Si(Si) ₄		Composition from NMR analysis
	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	
A	-107.6	42	-67.6	29	-31.3	11	-3.3	5	-15.2	13			SiC _{0.30} O _{1.40}
B	-108.8	36	-73.8	27	-37.0	11	-7.0	5	-16.4	21			SiC _{0.37} O _{1.25}
C	-109.7	67	-72.4	17	-39.6	5			-16.0	4	-85.0	7	SiC _{0.12} O _{1.77} + 0.06 Si

Table V. Chemical Analysis Characterization and Char Yields of Black Glasses Fired for 1 h at Various Temperatures between 1000° and 1500°C*

Pyrolysis parameters	Composition (wt%)			Empirical formula	Char yield (%)
	Si	C	O		
1000°C, 1 h	49.17	9.72	40.81	SiC _{0.46} O _{1.46}	100
1200°C, 1 h	48.88	10.18	40.79	SiC _{0.49} O _{1.46}	99.7
1400°C, 1 h	47.70	9.89	42.31	SiC _{0.48} O _{1.56}	
1500°C, 1 h	48.59	9.75	41.56	SiC _{0.47} O _{1.50}	97.5

*Hydrogen content, not reported here, was found to be lower than 0.30% for the 1000°C samples and lower than 0.15% for all of the other samples.

Chemical analysis and char yields reported in Table V show that the nominal composition of the black glass is stable up to 1500°C. However, in spite of this compositional stability, XRD analysis, reported in Fig. 5, suggests that, by increasing the firing temperature, a structural evolution occurs, leading to the crystallization of very fine β -SiC crystals. Indeed, starting from 1200°C, the typical diffraction peaks of cubic silicon carbide crystal around $2\theta = 35^\circ$, 60° , and 72° can be clearly seen. At 1500°C, an average crystallite size of ≈ 2 nm has been computed from the XRD data using the Scherrer equation.

The structural evolution shown by the XRD study is even more evident from the ^{29}Si MAS-NMR analysis reported in Fig. 6. By increasing the firing temperature, the intensity of the NMR signals due to mixed silicon oxycarbide units, especially SiCO_3 and SiC_2O_2 sites, progressively decreases, and finally the NMR spectrum at 1500°C shows mainly the resonance peaks due to SiO_4 ($\delta \approx -110$ ppm) and SiC_4 ($\delta \approx -15$ ppm) units. The NMR analysis clearly indicates that the starting homogeneous oxycarbide network undergoes structural rearrangements that lead to a phase separation into silica and silicon carbide, in agreement with the diffraction studies. A similar evolution has already been reported in the literature for different gel-derived oxycarbide glasses^{7,8,18,25} and has been ascribed¹⁸ to redistribution reactions between Si-O and Si-C bonds similar to those first discovered by Corriu *et al.*^{26,27} in a study on the pyrolysis of polysilsesquioxane gels. The NMR spectra have been simulated with individual components and the composition of the oxycarbide phase at various pyrolysis temperatures has been calculated (Table VI). The quantitative study suggests that, by increasing the temperature from 1000° to 1200°C, the oxycarbide network becomes richer in SiC_4 and SiO_4 units with a concurrent decrease of the amount of SiCO_3 and SiC_2O_2 units. It should be noted that this structural evolution occurs without any variation in the chemical composition of the oxycarbide phase as well as without any appreciable weight loss, as can be seen from the char yield reported in Table V. From 1200° to 1400°C, the relative amount of the various silicon units in the oxycarbide network is stable. Conversely, from 1400° to 1500°C, NMR analysis shows a dramatic decrease of the mixed SiCO_3 , SiC_2O_2 , and SiC_3O units and a simultaneous strong increase (from $\approx 18\%$ to $\approx 40\%$) of the silicon atoms in a silicon carbide environment, i.e., SiC_4 units. The peak due to these units has an asymmetric line shape and was simulated with three components at -16 , -20 , and -25 ppm. The first value is characteristic of Si sites present in crystalline β -SiC while the two others have been reported for α polytypes.²⁸ The presence of these three components has already been mentioned for SiC derived from polycarbosilane.²⁹ At this temperature, the composition of the oxycarbide network, derived from the NMR study, suggests that the amount of carbon atoms directly bonded to silicon atoms (C/Si) has increased from ≈ 0.29 at 1400°C up to ≈ 0.45 . This value is close to the total amount of carbon measured by chemical analysis, ≈ 0.47 . The NMR data have also been analyzed in terms of the number of Si-C and Si-O bonds per silicon atom (Fig. 7). The number of Si-C bonds is constant from 1000° to 1400°C, $\approx 1.2 \pm 0.1$, confirming the compositional stability of the oxycarbide phase. At 1500°C, the increase of the number of Si-C bonds up to $\approx 1.8 \pm 0.1$ seems to indicate that

some free carbon has reacted with the oxycarbide network to form new Si-C bonds.

Chemical analysis and ^{29}Si MAS-NMR results explicitly suggest the presence, in the pyrolyzed samples, of an extra C_{free} phase. While NMR investigation provided insight into the local order around the silicon atoms in terms of $\text{SiC}_x\text{O}_{4-x}$ ($0 \leq x \leq 4$) units and their evolution with the firing temperature, no information is available on the structure of the free carbon phase.

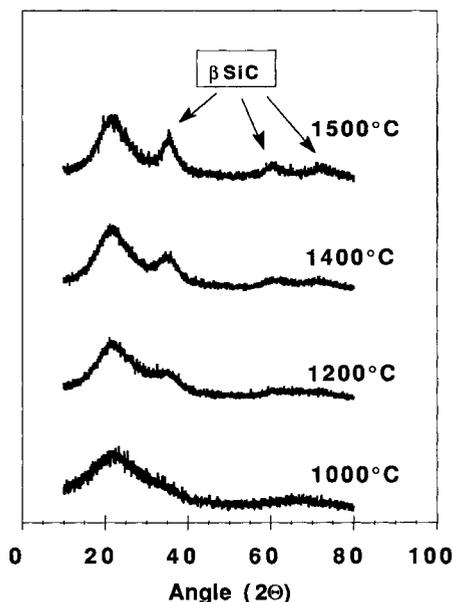


Fig. 5. XRD spectra recorded on sample A pyrolyzed for 1 h at various temperatures between 1000° and 1500°C.

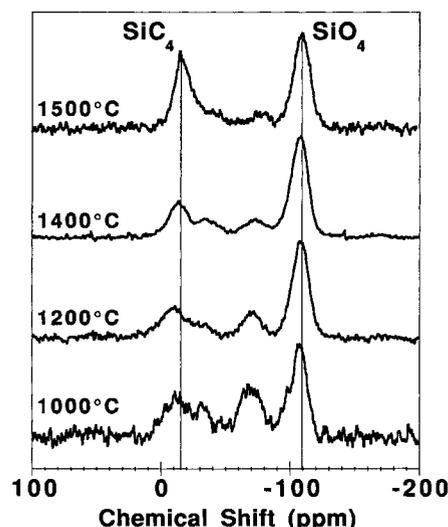
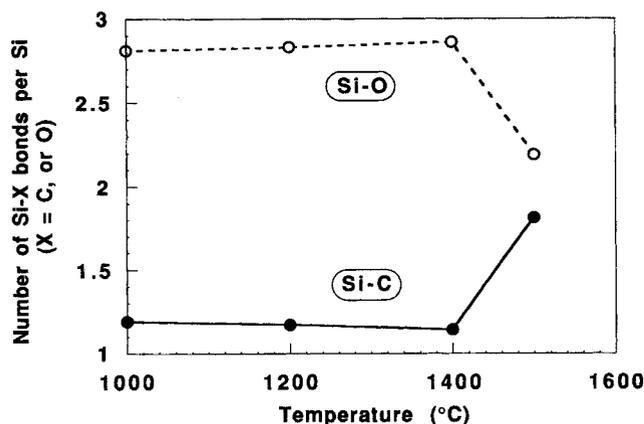


Fig. 6. ^{29}Si MAS-NMR spectra recorded on sample A pyrolyzed for 1 h at various temperatures between 1000° and 1500°C.

Table VI. Sample A: ^{29}Si MAS-NMR Characterization of Black Glass Fired for 1 h at Various Temperatures between 1000° and 1500°C

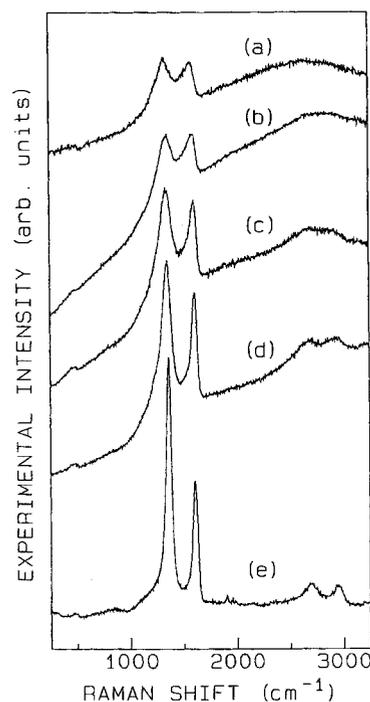
Pyrolysis parameters	SiO_4		SiCO_3		SiC_2O_2		SiC_3O		SiC_4		Composition from NMR analysis
	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	
1000°C, 1 h	-107.6	42	-67.6	29	-31.3	11	-3.3	5	-15.2	13	$\text{SiC}_{0.30}\text{O}_{1.40}$
1200°C, 1 h	-108.0	55	-72.0	15	-34.0	7	0.0	5	-10.6	18	$\text{SiC}_{0.29}\text{O}_{1.42}$
1400°C, 1 h	-108.0	54	-74.0	15	-36.0	12	-3.7	1	-14.2	18	$\text{SiC}_{0.29}\text{O}_{1.42}$
1500°C, 1 h	-110.7	47	-77.0	5	-42.0	7	-7.0	1	-16.5	40	$\text{SiC}_{0.45}\text{O}_{1.10}$

**Fig. 7.** Evolution of the average number of Si-C and Si-O bonds per Si sites units in sample A pyrolyzed for 1 h at various temperatures from 1000° to 1500°C.

This prompted us to study the pyrolysis process by Raman spectroscopy, which is the most suitable tool to characterize the various forms of crystalline as well as disordered graphitic carbons.³⁰ Typical Raman spectra recorded in the region 200–3200 cm^{-1} from oxycarbide glasses pyrolyzed at various temperatures between 1000° and 1500°C are shown in Fig. 8. Independently of the firing temperature, two main distinct features in the 1300–1600 cm^{-1} region are observed. They are superimposed upon a luminescence background whose spectral intensity and shape are strongly dependent on the processing temperature. For temperatures below 1300°C, the luminescence background whose maximum is around 2750 cm^{-1} (≈ 2.2 eV) is particularly broad and intense. In contrast, a nearly flat and relatively weak luminescence background is observed for samples fired at 1500°C. Such luminescence has already been reported for polymer-derived ceramics.^{8,18,31} This phenomenon could come from the presence of radical species. Indeed, the ESR spectrum of the sample fired at 1000°C shows a signal at $g = 2.0027$. Such a value, typical of organic free radicals, can be attributed to the presence of dangling bonds on C atoms.³² Similar ESR spectra have already been reported for polysilane-derived materials.^{29,33,34}

The pair of Raman bands observed in the 1300–1600 cm^{-1} region are the diagnostic features of all known disordered graphitic forms of carbon^{30,35–37} and are often referred to as the D and G bands,³⁰ respectively. In the highly disordered carbons, such as coke and charcoal, they are very broad bands whereas they turn out much more narrow in glassy carbon and in polycrystalline graphite. The higher energy band (G band) is the only vibrational mode (E_{2g} symmetry in the D_{6h}^4 space group) observed in this region for both natural single crystals of graphite^{30,36} and highly oriented pyrolytic graphite.^{30,37} The lower energy band (D band) occurs in the Raman spectra of carbon in polycrystalline and amorphous forms. The broadening of these bands relates to the degree of structural disorder of the graphitic phase.

The observation of the D and G bands in the Raman spectrum of the 1000°C sample clearly indicates the presence of a disordered graphitic-like component even at this temperature.

**Fig. 8.** Experimental Raman spectra obtained at room temperature under excitation of the 488.0-nm line from samples pyrolyzed for 1 h at (a) 1000°C, (b) 1200°C, (c) 1300°C, (d) 1400°C, and (e) 1500°C.

The band position and broadening change with firing temperature. In fact, their maxima continuously shift toward higher energies, from about 1323 and 1575 cm^{-1} in the spectrum of the 1000°C sample to the respective values of 1357 and 1605 cm^{-1} at 1500°C. As for their line broadening, a progressive narrowing is observed as a function of the pyrolysis temperature. The line-broadening evolution clearly suggests a structural rearrangement in the carbon phase which could occur through the growth or the ordering of existing nanocrystallites. The spectral parameters of these two bands derived from the spectra of the different samples are reported in Table VII. For the 1500°C sample, the Raman spectrum is very similar to that reported in the literature for turbostratic microcrystalline graphite and glassy carbon in which typical domain sizes are around 2 to 3 nm.^{35,38}

TEM studies confirmed the presence of a free carbon phase in the 1200° and the 1500°C samples derived from the gel A. Figure 9 shows a high-resolution micrograph of the sample fired at 1200°C in which a well-defined turbostratic graphite structure is clearly visible. Similar results were obtained for the 1500°C sample. The domain size of the turbostratic graphite structures was found to be usually lower than 5 nm with few crystallites, such as the one shown in Fig. 8, over 10 nm.

(4) Structural Characterization of Gels A, B, and C Fired at 1500°C: A Comparative Analysis

XRD spectra of the samples fired at 1500°C for 1 h are shown in Fig. 10. Samples A and B display similar spectra with the typical features of amorphous silica around $2\theta = 22^\circ$ and

Table VII. Sample A: Evolution of the Relative Intensity (I_D/I_G), Peak Frequency (ω), and Full Width at Half-Maximum (FWHM) of the D and G Bands with the Pyrolysis Temperature*

Pyrolysis parameters	I_D/I_G	ω_D (cm ⁻¹)	FWHM _D (cm ⁻¹)	ω_G (cm ⁻¹)	FWHM _G (cm ⁻¹)
1000°C, 1 h	1.36	1323	220	1575	96
1200°C, 1 h	1.38	1340	215	1590	86
1300°C, 1 h	1.31	1342	178	1605	70
1400°C, 1 h	1.36	1345	117	1605	72
1500°C, 1 h	1.92	1357	64	1605	61

*The parameters were derived from experimental Raman spectra shown in Fig. 7, after subtraction of the luminescence background.

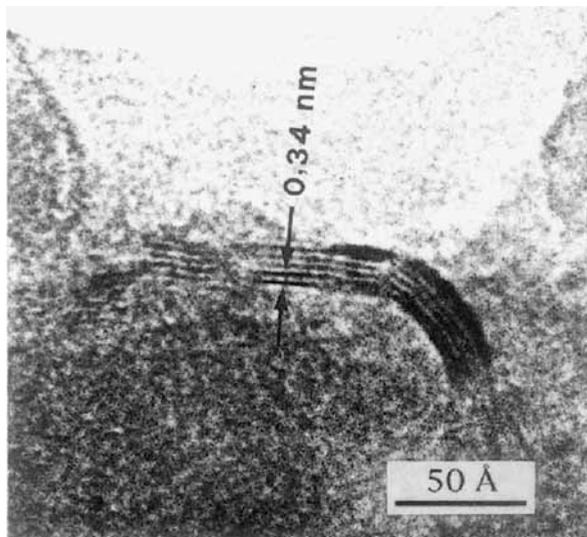


Fig. 9. High-resolution transmission electron micrograph of sample A fired at 1200°C showing a well-defined turbostratic graphite structure.

broad peaks at 35°, 60°, and 72° due to β -SiC microcrystals. The crystal size was estimated around 2 nm for both samples using a peak broadening procedure. The diffraction spectrum of sample C, besides the features of amorphous silica and cubic silicon carbide, shows also quite sharp peaks at $2\theta = 28^\circ, 50^\circ,$ and 55° due to the presence of a metallic silicon phase. Crystal sizes were estimated to be ≈ 3 nm for β -SiC and 20 nm for metallic silicon.

²⁹Si MAS-NMR spectra recorded on the same samples are shown in Fig. 11. They show two resonance peaks at ≈ -15 ppm and at ≈ -110 ppm, respectively, due to silicon atoms in silicon carbide and silica environments. In addition, the NMR spectrum of sample C shows a sharp peak at -79.4 ppm assigned to silicon atoms in a metallic silicon environment such as $Si(Si_4)$ units.

Thus NMR and XRD investigations explicitly indicate that for all of the studied samples, the amorphous oxycarbide phase formed at 1000°C undergoes, at 1500°C, a phase separation leading to the crystallization of β -SiC microcrystals into an amorphous silica phase. In order to extract quantitative information on the different phases present in the three 1500°C samples, the ²⁹Si MAS-NMR spectra have been simulated and the composition of the oxycarbide phases have been calculated (Table VIII). Results concerning sample A, showing at 1500°C an increase in the C content of the oxycarbide network, have already been presented above.

For sample B, it is worth noting that, at 1500°C, the stoichiometry of the oxycarbide phase derived from the NMR analysis ($SiC_{0.31}O_{1.38}$) is unchanged, within the accuracy of the experimental method, compared to the value at 1000°C ($SiC_{0.30}O_{1.39}$). This seems consistent with the absence, in this sample, of a free carbon phase. The weight loss between 1000° and 1500°C is

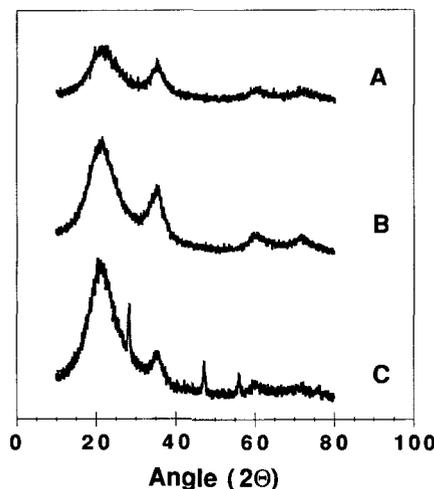


Fig. 10. XRD spectra recorded on samples A, B, and C pyrolyzed for 1 h at 1500°C.

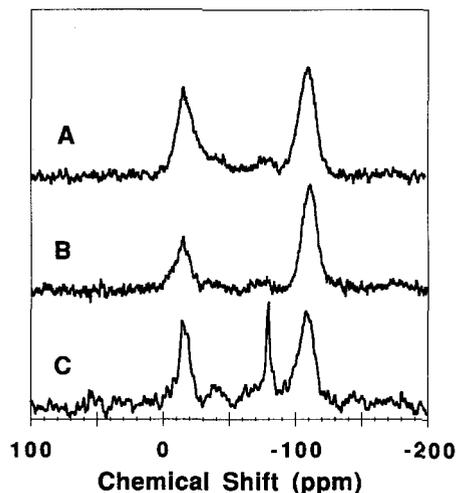


Fig. 11. ²⁹Si MAS-NMR spectra recorded on samples A, B, and C pyrolyzed for 1 h at 1500°C.

negligible ($\leq 2\%$). The chemical analysis gives the composition $SiC_{0.32}O_{1.43}$, in perfect agreement with the value at 1000°C ($SiC_{0.32}O_{1.39}$). This reveals the very high compositional stability of such samples even at 1500°C. NMR analysis of sample C at 1500°C reveals unambiguously the presence of a metallic silicon phase, as well as an oxycarbide phase with the composition $SiC_{0.35}O_{1.30}$. However, these quantitative results do not agree with the chemical analysis, which gives a much lower carbon content in the oxycarbide phase, $C/Si = 0.12$, similar to the value obtained at 1000°C.

Table VIII. ^{29}Si MAS-NMR Characterization of Black Glasses Fired for 1 h at 1500°C

Sample	SiO_4		SiCO_3		SiC_2O_2		SiC_2O		SiC_4		$\text{Si}(\text{Si})_4$		Composition from NMR analysis
	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	
A	-107.7	47	-72.4	5	-36.5	7	-7.0	1	-16.5	40			$\text{SiC}_{0.45}\text{O}_{1.10}$
B	-110.7	58	-74.4	8	-37.1	4	-8.5	12	-14.6	18			$\text{SiC}_{0.31}\text{O}_{1.38}$
C	-108.2	49	-67.2	6	-39.7	5			-15.7	26	-79.4	14	$\text{SiC}_{0.35}\text{O}_{1.30} + 0.16 \text{ Si}$

IV. Discussion and Conclusion

Gel precursors for silicon oxycarbide glasses have been prepared from cohydrolysis of triethoxysilane and methyl-diethoxysilane. The use of these two precursors allows us to vary the C/Si and O/Si contents in the starting gels. The studied compositions have been chosen in order to verify if the composition of the oxycarbide phase could be estimated from the composition of the starting gel, according to the model proposed in the introduction of this paper. The model is based on the assumption that the amount of oxygen does not change during the pyrolysis process, and therefore the stoichiometry of the oxycarbide network, $\text{SiC}_x\text{O}_{2(1-x)}$, can be directly obtained from the O/Si ratio in the starting gel. Three gels with the following theoretical compositions (estimated assuming fully condensed networks) have been studied: gel A, $\text{SiC}_{0.5}\text{O}_{1.25}\text{H}_{2.5}$; gel B, $\text{SiC}_{0.33}\text{O}_{1.33}\text{H}_{2.00}$; and gel C, $\text{SiC}_{0.09}\text{O}_{1.45}\text{H}_{1.27}$. Indeed, ^{29}Si MAS-NMR investigation and chemical analysis reveal that the hydrolysis-condensation reactions lead to the formation of fully condensed networks. Thus, according to the proposed model, the three gels should lead to the formation of the following oxycarbide phases: A, $\text{SiC}_{0.37}\text{O}_{1.25}$; B, $\text{SiC}_{0.33}\text{O}_{1.33}$; C, $\text{Si}_{0.81}\text{C}_{0.09}\text{O}_{1.45}$. The ^{29}Si NMR and chemical analyses give a description of the amorphous oxycarbide networks at 1000°C which are close to the expected ones. Indeed, for gels A and B, the (C/Si)_{oxy} ratio is in the range 0.30–0.37, and for gel C ≈ 0.12 . Moreover, as expected, NMR and chemical analysis seem to indicate, for sample C, the presence of Si–Si bonds, and for sample A, the formation of a free carbon phase. The Si–Si bonds present in the structure of the oxycarbide phase of the sample C fired at 1000°C give rise, at 1500°C, to a crystalline silicon phase as clearly shown by NMR and XRD studies. Moreover, a DTA analysis performed on the black glass C pyrolyzed at 1000°C (Fig. 12) shows an endothermic peak at $\approx 1450^\circ\text{C}$, assigned to the melting of the metallic silicon phase. When recorded on cooling, it shows an exothermic effect at $\approx 1300^\circ\text{C}$, related to the crystallization of the same phase.

^{29}Si MAS-NMR and chemical analysis experiments indicate that the pure oxycarbide phase obtained by pyrolysis of gel B at 1000°C undergoes a phase separation at 1500°C into microcrystalline β -SiC dispersed into an amorphous silica matrix. The quantitative NMR study suggests that the number of Si–C and Si–O bonds does not change during this process; therefore, the observed structural organization, which occurs without any weight loss, is not related to a carbothermal reduction process, but actually seems to be due to redistribution reactions between Si–C and Si–O bonds.

Black glass A, which consists of an oxycarbide matrix and a free carbon phase after pyrolysis at 1000°C, displays similar high-temperature behavior. Raman scattering results indicate that, since the lowest firing temperature, carbon is present in graphitic form and that a progressive structural ordering occurs at higher temperature. Such a structural rearrangement results in the formation of turbostratic or glassy carbon domains at 1500°C. XRD shows the crystallization of microcrystalline β -SiC and ^{29}Si MAS-NMR indicates the consumption of mixed silicon oxycarbide units with a phase separation into SiC_4 and SiO_4 sites. In this case, however, quantitative NMR analysis indicates, in the temperature range between 1400° and 1500°C, that the number of Si–C bonds increases with a corresponding consumption of Si–O bonds. This evolution could be related to a carbothermal reaction between the free carbon phase and the

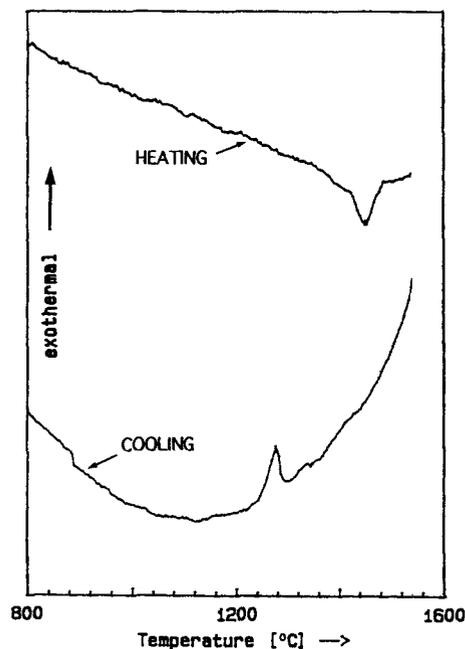
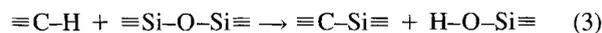


Fig. 12. DTA patterns, heating and cooling cycles, recorded on sample C previously fired at 1000°C for 1 h. Heating/cooling rate 10°C/min; Ar flow 100 cm³/min.

oxycarbide matrix with the formation of SiC and volatile species. Indeed, it is known from the literature³⁹ that the reaction



starts to be operative above 1300°C. Thus, assuming for sample A at 1000°C the composition estimated from the NMR analysis, i.e., $\text{SiC}_{0.30}\text{O}_{1.4} + 0.16\text{C}_{\text{free}}$, reaction (2) should lead to a weight loss of ≈ 5 wt%, close to the measured value of ≈ 2.5 %. However, even if this reaction is in agreement with the low level of weight loss, it cannot satisfactorily explain the rather high level of estimated carbon in the oxycarbide composition at 1500°C ($\text{SiC}_{0.45}\text{O}_{1.10}$). Actually, according to reaction (2), 0.16 mol of C_{free} can form 0.16/3 mol of SiC so that the expected composition should be $\text{SiC}_{0.35}\text{O}_{1.29}$. Assuming the presence of residual hydrogen as C–H groups, another possible reaction could be



This partial carbothermal reduction of Si–O bonds to form Si–C bonds could explain the observed increase of Si–C bonds with minimum weight loss. However, it should be a minor reaction due to the low hydrogen content (≤ 0.15 wt%; C/H ≈ 0.2) in the pyrolyzed samples.

Similar experimental data showing, in the temperature range 1400–1500°C, a weight stability and a simultaneous structural rearrangement leading to an increase of the number of Si–C bonds have already been reported in the literature^{7,8} for different gel-derived black glasses. This behavior is clearly different from what is usually reported for Nicalon fibers, in which an appreciable weight loss is observed in the temperature range 1200–1400°C, due to the carbothermal reduction of the oxycarbide phase present in the fiber.⁴⁰ The understanding of this discrepancy is under investigation.

Acknowledgments: We would like to acknowledge Jocelyne Maquet (Chimie de la Matière Condensée, Université P. et M. Curie, Paris) for her contribution to the MAS-NMR study and Mr. Michel Lavergne (Centre de Microscopie, Université P. et M. Curie, Paris) for the TEM pictures. Finally, we would like to thank Dr. E. Zanghellini for his skillful assistance in the Raman measurements and in the spectral analysis.

References

- ¹J. Homeny, G. G. Nelson, and S. H. Risbud, "Oxycarbide Glasses in the Mg-Al-Si-O-C System," *J. Am. Ceram. Soc.*, **71**, 386-90 (1987).
- ²G. M. Renlund, S. Prochazka, and R. H. Doremus, "Silicon Oxycarbide Glasses: Part II. Structure and Properties," *J. Mater. Res.*, **6**, 2723-34 (1991).
- ³G. D. Soraru, V. M. Sglavo, S. Dirè, G. D'Andrea, and F. Babonneau, "High-Strength, High-Modulus, Silicon Oxycarbide Glasses"; pp. 1157-62 in *Third Euro-Ceramics*, Vol. 2. Edited by P. Duran and J. F. Fernandez. Faenza Editrice Ibérica S. L., Spain, 1993.
- ⁴D. A. White, S. M. Oleff, R. D. Boyer, P. A. Budinger, and J. R. Fox, "Preparation of Silicon Carbide from Organosilicon Gels: I, Synthesis and Characterization of Precursor Gels," *Adv. Ceram. Mater.*, **2**, 45-52 (1987).
- ⁵D. A. White, S. M. Oleff, and J. R. Fox, "Preparation of Silicon Carbide from Organosilicon Gels: II, Gel Pyrolysis and SiC Characterization," *Adv. Ceram. Mater.*, **2**, 53-59 (1987).
- ⁶Y. Sugahara, Y. Takeda, K. Kuroda, and C. Kato, "The Preparation of Boron-Doped Silicon Carbide Powder by the Carbothermal Reduction of Oxides Derived from the Hydrolyzed Methyltriethoxysilane," *J. Non-Cryst. Solids*, **100**, 542-46 (1988).
- ⁷A. K. Singh and C. G. Pantano, "The Role of Si-H Functionality in Oxycarbide Glass Synthesis," *Mater. Res. Soc. Symp. Proc.*, **271**, 795-800 (1992).
- ⁸G. T. Burns, R. B. Taylor, Y. Xu, A. Zangvil, and G. A. Zank, "High-Temperature Chemistry of the Conversion of Siloxanes to Silicon Carbide," *Chem. Mater.*, **4**, 1313-23 (1992).
- ⁹R. Baney, "Some Organometallics Routes to Ceramics"; pp. 245-55 in *Ultrastructure Processing of Ceramics, Glasses, and Composites*. Edited by L. L. Hench and D. R. Ulrich. Wiley Interscience, New York, 1984.
- ¹⁰F. Babonneau, K. Thorne, and J. D. Mackenzie, "Dimethyldiethoxysilane/Tetraethoxysilane Copolymers: Precursors for the Si-C-O System," *Chem. Mater.*, **1**, 554-63 (1989).
- ¹¹H. Zhang and C. G. Pantano, "Synthesis and Characterization of Silicon Oxycarbide Glasses," *J. Am. Ceram. Soc.*, **73**, 958-63 (1990).
- ¹²R. M. Laine, K. A. Yougdahl, F. Babonneau, J. F. Harrod, M. L. Hoppe, and J. A. Rahn, "Synthesis and High-Temperature Chemistry of Methylsilsesquioxane Polymers Produced by Titanium-Catalyzed Redistribution of Methylhydrido-oligo- and -polysiloxanes," *Chem. Mater.*, **2**, 464-72 (1990).
- ¹³K. Kamiya, T. Yoko, T. Sano, and K. Tanaka, "Distribution of Carbon Particles in Carbon/SiO₂ Glass Composites Made from CH₃Si(OC₂H₅)₃ by the Sol-Gel Method," *J. Non-Cryst. Solids*, **119**, 14-20 (1990).
- ¹⁴K. Kamiya, T. Yoko, K. Tanaka, and M. Takeuchi, "Thermal Evolution of Gels Derived from CH₃Si(OC₂H₅)₃ by the Sol-Gel Method," *J. Non-Cryst. Solids*, **121**, 182-87 (1990).
- ¹⁵G. M. Renlund, S. Prochazka, and R. H. Doremus, "Silicon Oxycarbide Glasses: Part I. Preparation and Chemistry," *J. Mater. Res.*, **6**, 2716-22 (1991).
- ¹⁶F. Babonneau, L. Bois, and J. Livage, "Silicon Oxycarbides via Sol-Gel Route: Characterization of the Pyrolysis Process," *J. Non-Cryst. Solids*, **147-148**, 280-84 (1992).
- ¹⁷V. Belot, R. J. P. Corriu, D. Leclercq, P. H. Mutin, and A. Vioux, "Organosilicon Gels Containing Silicon-Silicon Bonds, Precursors to Novel Oxycarbide Compositions," *J. Non-Cryst. Solids*, **144**, 287-97 (1992).
- ¹⁸F. Babonneau, G. D. Soraru, G. D'Andrea, S. Dirè, and L. Bois, "Silicon-Oxycarbide Glasses from Sol-Gel Precursors," *Mater. Res. Soc. Symp. Proc.*, **271**, 789-94 (1992).
- ¹⁹F. I. Hurwiz, P. Heimann, S. C. Farmer, and D. M. Hembree, Jr., "Characterization of the Pyrolytic Conversion of Polysilsesquioxanes to Silicon Oxycarbides," *J. Mater. Sci.*, **28**, 6622-30 (1993).
- ²⁰F. Babonneau, L. Bois, C.-Y. Yang, and L. Interrante, "Sol-Gel Synthesis of a Siloxypolycarbosilane Gel and Its Pyrolytic Conversion to Silicon Oxycarbide," *Chem. Mater.*, **6**, 51-57 (1994).
- ²¹L. Bois, J. Maquet, F. Babonneau, H. Mutin, and D. Balhoul, "Structural Characterization of Sol-Gel Derived Oxycarbide Glasses. I—Study of the Pyrolysis Process," *Chem. Mater.*, **6**, 796-802 (1994).
- ²²G. D. Soraru, "Silicon Oxycarbide Glasses from Gels"; in *Sol-Gel Science and Technology*, **2**, 843-48 (1994).
- ²³F. Babonneau, G. D. Soraru, G. D'Andrea, and D. Balhoul, "Importance of Si-H Bonds in the Conversion Process of Methyl-substituted Silica Gels into Silicon Oxycarbide Glasses," in preparation.
- ²⁴J. S. Hartman, M. F. Richardson, B. L. Sherriff, and B. G. Winsborrow, "Magic Angle Spinning NMR Studies of Silicon Carbide: Polytypes, Impurities, and Highly Inefficient Spin-Lattice Relaxation," *J. Am. Chem. Soc.*, **109**, 6059-67 (1987).
- ²⁵H. Zhang and C. G. Pantano, "High Temperature Stability of Oxycarbide Glasses," *Mater. Res. Soc. Symp. Proc.*, **271**, 783-88 (1992).
- ²⁶V. Belot, R. J. P. Corriu, D. Leclercq, P. H. Mutin, and A. Vioux, "Redistribution Reactions in Silsesquioxane Gels," *J. Mater. Sci. Lett.*, **9**, 1052-54 (1990).
- ²⁷V. Belot, R. J. P. Corriu, D. Leclercq, P. H. Mutin, and A. Vioux, "Thermal Redistribution Reactions in Cross-Linked Polysiloxanes," *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 613-23 (1992).
- ²⁸J. R. Guth and W. T. Petruskey, "Silicon-29 Magic Angle Spinning Nuclear Magnetic Resonance Characterization of SiC Polytypes," *J. Phys. Chem.*, **91**, 5361-64 (1987).
- ²⁹G. D. Soraru, F. Babonneau, and J. D. Mackenzie, "Structural Evolution from Polycarbosilane to SiC Ceramics," *J. Mater. Sci.*, **25**, 3886-93 (1990).
- ³⁰D. S. Knight and W. B. White, "Characterization of Diamond Films by Raman Spectroscopy," *J. Mater. Res.*, **4**, 385-93 (1989).
- ³¹Y. Sasaki, Y. Nishina, M. Sato, and K. Okamura, "Raman Study of SiC Fibres Made from Polycarbosilane," *J. Mater. Sci.*, **22**, 443-48 (1987).
- ³²B. Marshik, D. Meyer, and T. Apple, "Electron-Spin-Resonance Studies of Vapor-Grown Carbon Fibers," *J. Appl. Phys.*, **62**, 3947 (1987).
- ³³W. R. Schmidt, L. V. Interrante, R. H. Doremus, T. K. Trout, P. S. Marchetti, and G. E. Maciel, "Pyrolysis Chemistry of an Organometallic Precursor to Silicon Carbide," *Chem. Mater.*, **3**, 257-67 (1991).
- ³⁴J. Lipowitz and G. L. Turner, pp. 305-20 in *Solid State NMR of Polymers*. Edited by L. Mathias. Plenum Press, New York, 1991.
- ³⁵R. J. Nemanich and S. A. Solin, "First- and Second-Order Raman Scattering from Finite-Size Crystals of Graphite," *Phys. Rev. B*, **20**, 392-401 (1979).
- ³⁶F. Tuinstra and L. L. Koenig, "Raman Spectrum of Graphite," *J. Chem. Phys.*, **53**, 1126-30 (1970).
- ³⁷Y. Yang, D. C. Alsmeyer, and R. L. McCreery, "Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra," *Chem. Mater.*, **2**, 557-63 (1990).
- ³⁸M. I. Nathan, J. E. Smith, Jr., and K. N. Tu, "Raman Spectra of Glassy Carbon," *J. Appl. Phys.*, **45**, 2370 (1974).
- ³⁹D. H. Filsinger and D. B. Bourrie, "Silica to Silicon: Key Carbothermal Reactions and Kinetics," *J. Am. Ceram. Soc.*, **73**, 1726-32 (1990).
- ⁴⁰Y. Hasegawa, "Synthesis of Continuous Silicon Carbide Fibre. Part 6, Pyrolysis Process of Cured Polycarbosilane Fibers and Structure of SiC Fibers," *J. Mater. Sci.*, **24**, 1177-90 (1989). □