

# Chemical Durability of Silicon Oxycarbide Glasses

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**Silicon oxycarbide (SiOC) glasses with controlled amounts of Si—C bonds and free carbon have been produced via the pyrolysis of suitable preceramic networks. Their chemical durability in alkaline and hydrofluoric solutions has been studied and related to the network structure and microstructure of the glasses. SiOC glasses, because of the character of the Si—C bonds, exhibit greater chemical durability in both environments, compared with silica glass. Microphase separation into silicon carbide (SiC), silica (SiO<sub>2</sub>), and carbon, which usually occurs in this system at pyrolysis temperatures of >1000–1200°C, exerts great influence on the durability of these glasses. The chemical durability decreases as the amount of phase separation increases, because the silica/silicate species (without any carbon substituents) are interconnected and can be easily leached out, in comparison with the SiOC phase, which is resistant to attack by OH<sup>−</sup> or F<sup>−</sup> ions.**

## I. Introduction

PRECERAMIC precursor pyrolysis is a relatively new processing method for the production of advanced ceramics.<sup>1</sup> It is well suited for the synthesis of binary or multicomponent systems, such as SiC, Si<sub>3</sub>N<sub>4</sub>, SiOC, SiNC, SiBCN, etc. According to this process, the starting material is a polymer or alkoxide that, first, is shaped, then crosslinked and/or gelled, and finally converted to the desired ceramic component through a pyrolysis process in an inert atmosphere at temperatures of >800°C. Among the many advantages of this processing route is the possibility of producing very complex nanostructures in which nanocrystalline phases (such as SiC or Si<sub>3</sub>N<sub>4</sub>), unique amorphous phases (e.g., SiOC or SiNC), and a free-carbon phase coexist. It is believed that the unusual properties that have been observed for these materials—such as an exceptionally low creep rate<sup>2</sup> and high thermal stability<sup>3</sup>—can be, at least partially, attributed to this complex nanostructure. The

free-carbon phase especially has an important role in the stability of amorphous and nanocrystalline phases.<sup>4</sup>

Among the various precursor-derived ceramic systems, silicon oxycarbide glasses<sup>5</sup> can be produced from preceramic networks that have been obtained either by cross-linking silicone polymers<sup>6</sup> or via the hydrolysis–condensation of hybrid silicon alkoxides through the sol–gel process.<sup>7</sup> The structure of the SiOC glass obtained after pyrolysis at 800°–1000°C has been extensively characterized, mainly by <sup>29</sup>Si magic-angle spinning nuclear magnetic resonance (<sup>29</sup>Si MAS NMR) analysis; the structure is based on a random network of Si—O and Si—C bonds in which all the possible Si sites (SiC<sub>4</sub>, SiOC<sub>3</sub>, SiO<sub>2</sub>C<sub>2</sub>, SiO<sub>3</sub>C, SiO<sub>4</sub>) can be found in different ratios with the free-carbon phase.<sup>8–10</sup> For this reason, its composition is usually reported as follows:

$$\text{Composition of silicon oxycarbide} = \text{SiC}_x\text{O}_{2(1-x)} + y\text{C}_{\text{free}} \quad (1)$$

where SiC<sub>x</sub>O<sub>2(1-x)</sub> describes the amorphous silicon oxycarbide network and C<sub>free</sub> is free carbon. Moreover, SiC<sub>x</sub>O<sub>2(1-x)</sub> can be rewritten as xSiC + (1 - x)SiO<sub>2</sub> and one can consider the x value in the silicon oxycarbide formula to be a direct measure of the relative amount of SiC and SiO<sub>2</sub> that would be present for the analogous equilibrium assemblage. In fact, at temperatures of >1000°–1200°C, silicon oxycarbide glasses usually undergo a phase transformation wherein an equilibrium between this multiphase mixture of SiC, (turbostratic) carbon, and SiO<sub>2</sub> (usually cristobalite) is eventually attained.<sup>4</sup> During the course of this transformation, nanocrystals of SiC and carbon appear in a matrix of amorphous SiO<sub>2</sub> or SiOC phase.<sup>11,12</sup> In the preceramic literature, this structural and compositional rearrangement is often called a “phase separation,”<sup>12</sup> and we will adopt this terminology in the remainder of the text.

In oxynitride glasses, N atoms are three-coordinated by Si atoms, which increases the level of network crosslinking, with respect to pure oxide glasses. The density, viscosity (and glass-transition temperature), microhardness, elastic modulus, fracture toughness, and refractive index of nitrogen glasses all increase, whereas the thermal expansion decreases because of the replacement of O atoms by N atoms in the glass structure.<sup>13</sup> Similarly, the chemical durability of oxynitride glasses, in water<sup>14</sup> or alkaline solutions,<sup>15</sup> is better than that of borosilicate, soda-lime, or silica glass under those conditions; an increase in durability, relative to the nitrogen content, has been observed. All these property changes are attributed to the fact that the structure of SiON glasses is denser than that of the analogous oxide glasses.

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A similar change in property values can be expected for oxycarbide glasses and has, indeed, been observed in the mechanical properties,<sup>6b,16,17</sup> creep behavior,<sup>18,19</sup> and high-temperature stability.<sup>11,20</sup> A small amount of data is available concerning properties such as high-temperature oxidation resistance,<sup>21</sup> electrical conductivity, and dielectric constant.<sup>22,23</sup> In the case of chemical durability, the HF resistance of SiOC glasses has been noted;<sup>24–26</sup> but otherwise, the reactions of these glasses in aqueous solutions have never been reported in the literature.

The present investigation focuses on the chemical durability of SiOC glasses in highly basic or acidic (HF) solutions. These conditions are those under which SiO<sub>2</sub> and silicate glasses are normally quite soluble.<sup>27</sup> SiOC glasses with different amounts of bonded and free carbon (values  $x$  and  $y$ , respectively, in Eq. (1)) have been produced and studied for the purpose of establishing the role of the Si—C bonds and the free-carbon phase in the leaching and dissolution behavior. Moreover, the role of the microstructure (homogeneous versus phase-separated glass), relative to the chemical durability, is also considered.

## II. Experimental Procedure

Two of the four SiOC glasses used in this study were obtained via the sol–gel method. The sample labeled “T<sup>H</sup>/D<sup>H</sup> 2/1” was produced via the co-hydrolysis of triethoxysilane (HSi(OEt)<sub>3</sub>) and methyl-diethoxysilane (HMeSi(OEt)<sub>2</sub>) in a 2:1 ratio. The alkoxides (from ABCR, Karlsruhe, Germany) were dissolved in ethanol (EtOH/Si = 2) and hydrolyzed with water (H<sub>2</sub>O/OR = 1, pH 4.70 by HCl). Hydrolysis was conducted in an ice bath, to reduce the hydrolysis rate. The solution was stirred for 20 min and then poured into open test tubes for gelation. Monolithic and transparent gel samples were obtained after a drying process of 10 d from 40°C to 110°C, in steps of 20°C every 2 d.

The second sol–gel system (labeled “MTES”) was produced from methyltriethoxysilane (also from ABCR). In this case, hydrolysis was conducted at 70°C with a stoichiometric amount of acidic water (H<sub>2</sub>O/OR = 1; pH 1 by HCl). After the water addition, the solution was maintained at 70°C for 20 min and then poured into open tubes. The other two glasses used for this study were derived from commercial polysiloxane resins (Products SR350 and SR355, General Electric Silicone Products Division, Waterford, NY; SR350 was a methyl-substituted resin and SR355 was a methyl/phenyl-substituted resin). These preceramic polymers were cross-linked before pyrolysis by heating at 150°C for 4 h in air.

All four of these SiOC precursors were transformed to SiOC glasses via a pyrolysis process in a flowing argon atmosphere (flow rate of 100 cm<sup>3</sup>/min) at different temperatures (1000°, 1200°, and 1400°C). The pyrolysis was conducted by placing the sample in a graphite crucible and then a graphite furnace (Astro furnace, Thermal Technology, Inc., Santa Barbara, CA); a heating rate of 5°C/min was used, with a holding time of 1 h at the maximum temperature. The fragmented SiOC glasses obtained after pyrolysis were ground and sieved to obtain fine powders (with diameters of 80–224 μm) to be used in the durability tests. Thin SiOC disks for selected durability tests on bulk samples were produced via the pyrolysis of gel disks (obtained by sectioning the original monolithic gels).

Two different types of vitreous silica, and a commercial soda-lime glass, were used as reference materials to interpret these chemical-durability results. Fused silica glasses (Suprasil 300 and 2, Heraeus Quarzglas, Hanau, Germany) with different amounts of hydroxyl groups (<1 and <1000 ppm, respectively) were tested. The composition of the soda-lime glass was 72 wt% SiO<sub>2</sub>, 1.6 wt% Al<sub>2</sub>O<sub>3</sub>, 13.2 wt% Na<sub>2</sub>O + K<sub>2</sub>O, and 13.0 wt% CaO + MgO.

The chemical durability of the SiOC glasses was studied in basic and acidic (HF) media using Teflon<sup>TM</sup> (Dupont, Wilmington, DE) containers. For the basic resistance test, 1 g of powdered glass was introduced into 60 mL of solution that was prepared with 30 mL of 0.5M Na<sub>2</sub>CO<sub>3</sub> and 30 mL of 1M NaOH (pH 12.3). The concentration of the alkaline solution was selected to match the

composition of the extractant used for commercial glasses under standard testing conditions.<sup>†</sup> The test was conducted at 80°C for 2 h. No reference methods were available in the literature to test the glass resistance to HF. Therefore, an ad hoc procedure was developed: 1 g of powdered glass was placed in 60 mL of a 5%-vol-HF solution and continuously stirred at room temperature for 15 min.

In both cases, the powders were separated by filtration, after careful washing with distilled water, and the washings were gathered to the main extraction solution. The silica content in the extract was measured via flame absorption spectroscopy (Model Spectra AA200, Varian, Palo Alto, CA).

All X-ray photoelectron spectroscopy (XPS) analyses were performed using a spectrometer (Model XSAM 800, Kratos Analytical, Wharfedale, Manchester, U.K.) with an achromatic MgKα radiation source (1253.6 eV). C 1s, Si 2p, and O 1s spectra were collected, with a step size of 0.1 eV and an energy of 40 eV per pass; the analyzed area was fixed at 700 μm (iris fully open). The binding energies were charge-referenced to the O 1s peak at 532.2 eV. All the samples were exposed to ozone in an ultraviolet ozone cleaner (UVOC) for 15 min, to remove organic contaminants before XPS analysis. Quantification of the data involved calculating atomic percentages with sensitivity factors that were calibrated against a poly(dimethylsiloxane) (PDMS) standard. Curve fitting of the high-resolution spectra was conducted using a commercial software package. Two peaks were necessary to fit the Si 2p spectra; the details are reported elsewhere.<sup>26</sup>

The oxycarbide glasses were analyzed for silicon, carbon, and hydrogen contents by the service d'Analyse Elementaire du CNRS, France. The oxygen content was calculated by difference.

A diffractometer (Model D-max B, Rigaku, Tokyo, Japan) operated at 40 kV and 30 mA was used to record the XRD spectra of powder samples that were fired at various temperatures. The spectra were collected in the 2θ range of 10°–110°, with a step of 0.05° every 5 s.

The specific surface area (SSA) measurements were performed (Model ASAP 2010, Micromeritics, Norcross, GA) on SiOC glasses before and after the durability tests. Nitrogen specific surface areas at a temperature of 77 K were determined from a Brunauer–Emmett–Teller (BET) analysis in the  $P/P_0$  range of 0.05–0.30, using a molecular cross-sectional area of 0.163 nm<sup>2</sup>. These measured surface areas were used to verify that the pyrolyzed glasses were fully dense and to normalize the dissolved silica concentrations for the durability tests.

To gain insight into the structure of the free-carbon phase, room-temperature micro-Raman spectra were recorded on powdered samples before and after leaching. The samples were excited in air with an argon-ion laser that was operating at 488.0 nm in a 90° scattering geometry. The scattered radiation was dispersed with a double monochromator (Model Ramanor HG2-S, Jobin-Yvon, Longjumeau, France) that was equipped with holographic gratings, and the radiation was detected with a cooled photomultiplier that was interfaced with a standard photon counting system.

The morphology of the glass surfaces, before and after leaching, was investigated using techniques that involved scanning electron microscopy (SEM) (Model JSM-6300, JEOL, Tokyo, Japan) and atomic force microscopy (AFM) (Burleigh Instruments). For this purpose, bulk MTES-derived SiOC glasses (thin disks) were produced via pyrolysis at 1200°C. Both fused silica and SiOC disks were polished with 1 μm diamond paste, using dried ethanol as a lubricant, before the test.

## III. Experimental Results

### (I) Chemical Analysis and (Micro)structural Characterization

Chemical analyses were performed on the various SiOC glasses and are reported in Table I, together with the measured char yield.

<sup>†</sup>ISO Standard Test Method 695, “Resistance to Attack by a Boiling Aqueous Solution of Mixed Alkali—Method of Test and Classification,” International Organization for Standardization, Geneva, Switzerland, 1991.

**Table I. Chemical Composition and Char Yield of the Studied SiOC Glasses**

Temperature (°C)	Yield (%)	Composition (wt%)			Empirical formula	Oxycarbide stoichiometry	Amount of component (vol%)	
		Silicon	Carbon	Oxygen			SiC	Carbon
					$T^H/D^H$ 2/1			
1000	88.2	51.09	7.55	41.36	$SiC_{0.35}O_{1.48}$			
1200	91.5	51.94	6.96	41.10	$SiC_{0.31}O_{1.39}$	$SiC_{0.30}O_{1.39} + 0.01C$	16.6	0.2
1400	70.3	51.53	7.43	40.72	$SiC_{0.33}O_{1.39}$	$SiC_{0.30}O_{1.39} + 0.04C$	16.8	0.9
					MTES			
1000	85.9	43.30	14.06	42.64	$SiC_{0.76}O_{1.72}$			
1200	85.9	46.32	13.50	40.18	$SiC_{0.68}O_{1.51}$	$SiC_{0.24}O_{1.51} + 0.44C$	11.5	9.0
1400	74.6	46.12	14.46	39.22	$SiC_{0.73}O_{1.49}$	$SiC_{0.26}O_{1.49} + 0.47C$	12.5	9.6
					SR350			
1000	82.1	42.60	14.17	43.23	$SiC_{0.78}O_{1.77}$			
1200	80.9	46.66	13.66	39.68	$SiC_{0.68}O_{1.49}$	$SiC_{0.25}O_{1.49} + 0.43C$	12.3	8.8
1400	78.3	44.68	14.06	41.26	$SiC_{0.73}O_{1.61}$	$SiC_{0.20}O_{1.61} + 0.53C$	9.1	10.4
					SR355			
1000	82.2	39.75	34.33	25.38	$SiC_{2.28}O_{1.50}H_{0.38}$			
1200	80.2	34.11	32.70	33.19	$SiC_{2.24}O_{1.71}$	$SiC_{0.15}O_{1.71} + 2.09C$	5.2	30.6

Except for the SR355-derived SiOC sample that was obtained at 1000°C, the hydrogen content was always <0.3 wt% (i.e., at the detection limit of the technique), so it is not reported in the formula. However, one should recall that the hydrogen content at 1000°C is not negligible. Indeed, thermal analysis/emission gas analysis (TA/EGA) experiments on SiOC glasses usually indicate the evolution of hydrogen gas at >1000°C and up to 1200°C.<sup>28</sup> The SR355 resin, when pyrolyzed at 1400°C, decomposes because of carbothermal reduction reactions;<sup>11</sup> accordingly, SR355 has been studied only up to a maximum temperature of 1200°C. This effect is mainly due to its high amount of free carbon, which decreases the high-temperature stability of SiOC glasses.<sup>20</sup>

To facilitate the discussion of chemical durability in terms of the content of bonded and free carbon, the chemical compositions of the 1200°C and 1400°C SiOC glasses have also been expressed according to Eq. (1):  $SiC_xO_{2(1-x)} + yC_{free}$  in Table I. Moreover, the equivalent volume percentage of SiC and free carbon is reported. On the other hand, for the samples annealed at 1000°C, the presence of CH or CH<sub>2</sub> groups is believed to prevent the description of the material in terms of a fully condensed silicon oxycarbide glass ( $SiC_xO_{2(1-x)}$ ) and a dehydrogenated carbon phase (free carbon,  $C_{free}$ ). Thus, no stoichiometric formula has been suggested in Table I for the 1000°C materials.

The data reported in Table I clearly indicate that (i) the total amount of carbon in the SiOC glasses increases at every pyrolysis temperature, going from  $T^H/D^H$  2/1 to MTES to SR355 (also see the empirical formula); (ii) MTES and SR350 samples have the same chemical composition, in accordance with the similarity in the chemical structure of their condensed networks; (iii) the amount of bonded carbon, i.e., the  $x$  value in the oxycarbide stoichiometry or the volume percentage of SiC, decreases from  $T^H/D^H$  2/1 to MTES to SR355; (iv) the amount of free carbon, i.e. the  $y$  value in the oxycarbide stoichiometry or the volume percentage of carbon, increases from  $T^H/D^H$  2/1 to MTES to SR355; and (v) for each sample, the composition does not change considerably from 1200°C to 1400°C. Also, one should note that all the glasses showed specific surface area (SSA) values of <1 m<sup>2</sup>/g, which indicates the absence of open porosity and the formation of a dense material.

The corresponding phase state of these SiOC glasses has been characterized using XRD (see Fig. 1). SiOC glasses obtained at 1000°C display a typical amorphous diffraction pattern, with just one broad halo centered at  $2\theta \approx 22^\circ$ . Only in the spectrum of  $T^H/D^H$  2/1 does a small shoulder present itself, at  $2\theta \approx 35^\circ$ . At 1200°C, this shoulder grows and two more peaks appear—at  $2\theta \approx 60^\circ$  and  $72^\circ$ —which allows precise assignment to the formation of cubic  $\beta$ -SiC nanocrystals. The average crystallite size, as estimated by the Scherrer equation, is 1.7 nm ( $\pm 10\%$ ). The XRD

spectra of the 1200°C MTES-derived glass show a similar pattern; however, the diffraction peaks are broader. In this case, the average crystallite size is  $\sim 1$  nm ( $\pm 10\%$ ), which suggests that the crystallization process is less pronounced in comparison with the  $T^H/D^H$  2/1 glass. Interestingly, the 1200°C SiOC glass that was derived from SR350, despite having the same chemical composition of the MTES sample, is still amorphous. Similarly, the SiOC glass that was derived from SR355 is still amorphous at 1200°C. This stability against crystallization is attributed to their higher carbon contents.

At 1400°C, all the glasses transform to  $\beta$ -SiC nanocrystals in a phase-separated silica/silicon oxycarbide-based amorphous matrix. The estimated average  $\beta$ -SiC crystallite sizes are 2.2, 1.4, and 1.2 nm ( $\pm 10\%$  nm) for  $T^H/D^H$  2/1, MTES, and SR350, respectively. These results are consistent with the idea that the presence of free carbon hinders the phase-separation process (which is more pronounced for the stoichiometric glass). This effect of carbon on the crystallization of  $\beta$ -SiC in precursor-derived ceramics has been reported several times in the literature<sup>18,29</sup>

The structure and domain size of the free-carbon phase have been obtained from a Raman study performed on the SiOC samples that were pyrolyzed at 1200°C (a typical spectrum is reported in Fig. 2).<sup>30</sup> In all these samples, the presence of D and G bands in the Raman spectra at  $\sim 1350$  and  $1600$  cm<sup>-1</sup> clearly indicates the existence of a disordered graphitic-like component.<sup>31</sup> The intensity ratio of the two bands is inversely proportional to the domain size.<sup>32</sup> Accordingly, the average “graphite” crystallite size estimated from this Raman data are  $\sim 1.5$  nm for the  $T^H/D^H$  2/1 and MTES samples and  $\sim 3.5$  nm for the SR 350 and 355 samples.

## (2) Leaching Tests

Results of the leaching tests, in both basic and HF solutions, are reported in Table II. The raw data, expressed as milligrams of SiO<sub>2</sub> per gram of glass ( $mg_{SiO_2}/g_{glass}$ ), have been normalized by dividing them by the SSA (given in units of m<sup>2</sup>/g) and by the relative amount of silicon and oxygen in the SiOC glass (expressed as grams of silicon and oxygen per gram of glass,  $(g_{Si} + g_O)/g_{glass}$ ). Therefore, the durability values are expressed as  $mg_{SiO_2}/[m^2(g_{Si} + g_O)/g_{glass}]$ . The error in these latter durability tests is rather high ( $\sim 30\%$ ), mainly because of the uncertainty in the SSA measurements. Nevertheless, the leaching tests reveal a clear trend.

The data show that all the SiOC glasses are more resistant to strong basic or HF solutions than are pure SiO<sub>2</sub> and soda-lime glasses. Indeed, the specific durability values measured for all the SiOC glasses are less than those for fused silica and soda-lime glasses, except for the  $T^H/D^H$  2/1-derived glass at 1000°C. In some

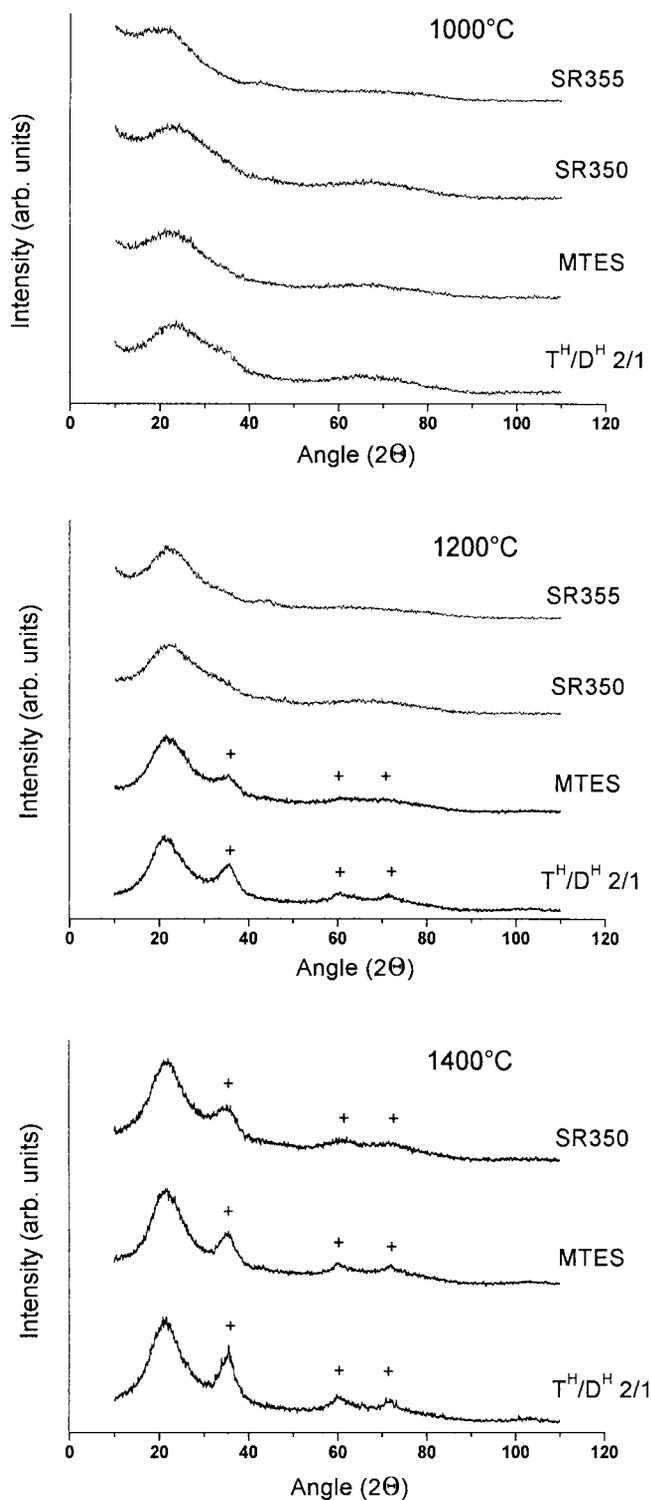


Fig. 1. XRD patterns for samples pyrolyzed at 1000°, 1200°, and 1400°C. (Peaks attributable to  $\beta$ -SiC are noted with a cross (+).)

cases, the chemical durability of the SiOC glass is one or two orders of magnitude higher than the reference glasses.

### (3) Effects of Leaching on (Surface) Chemical Structure

The changes in surface composition that are induced by the leaching process are revealed in XPS spectra that have been recorded before and after the durability tests in alkaline solution (Table III). The XPS spectra recorded on the 1200°C samples before leaching show the presence of Si, C, and O atoms. The  $\text{Si}_{2p}$

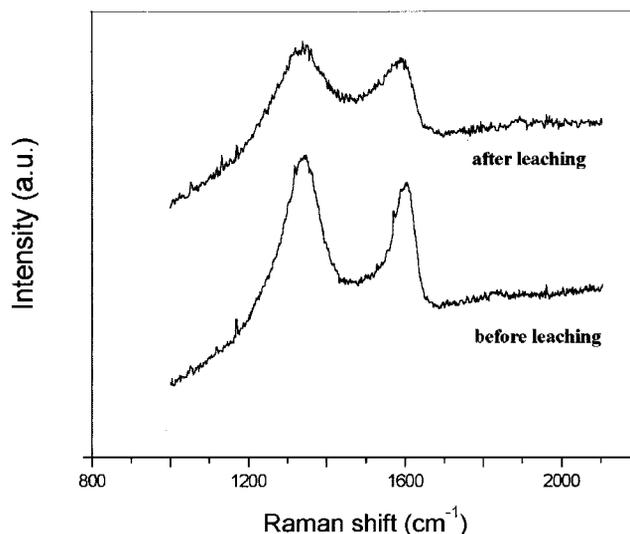


Fig. 2. Experimental Raman spectra obtained at room temperature under excitation of the 488.0 nm line from SR350-derived SiOC glasses, pyrolyzed at 1200°C, before and after leaching in alkaline solution.

peak always contains two components: one component with a binding energy (BE) of  $\sim 100$  eV ( $\text{Si}^1$ ), which is due to Si atoms simultaneously bonded to O and C atoms in the silicon oxycarbide phase, and one component with a BE value of  $\sim 102.5$  eV ( $\text{Si}^2$ ), which is assigned to the Si atoms in silica.<sup>26</sup> This deconvolution of the  $\text{Si}_{2p}$  peaks provides an estimate of the relative amounts of silicon in the SiOC and  $\text{SiO}_2$  phases. Altogether, the data reported in Table III for the various SiOC glasses are consistent with the bulk chemical analysis reported in Table I. In particular, they show that (i) the amount of carbon decreases from  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1 to MTES to SR355; (ii) the composition of MTES- and SR350-derived materials are the same, within the experimental error; and (iii)  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1 glass has the highest amount of SiOC phase, whereas the SR355 has the lowest SiOC content. Most importantly, Table III shows that the leaching process preferentially depletes the glass structure of the Si atoms that are associated with the pure silica phase (or silicate species). Similarly, a consistent increase in the relative concentration of carbon after leaching occurs. Especially interesting is the fact that, in the  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1- and MTES-derived materials, the increase in carbon is accompanied by a corresponding increase in the relative concentration of Si—C bonds (as revealed in the  $\text{Si}^1$  peak). This phenomenon is not the case for the SR350- and SR355-derived materials; instead, an increase in the amount of carbon is observed, as well as a decrease in the relative concentration of both types of silicon species.

## IV. Discussion

$^{29}\text{Si}$  MAS NMR for the SiOC samples annealed at 1000°C have been already reported in the literature; this analysis proves the formation of the expected amorphous silicon oxycarbide glass.<sup>6,7,33</sup> The XRD analysis conducted in this work (Fig. 1) shows that all the SiOC samples at 1000°C are amorphous; this finding is consistent with the NMR study. The degree of phase separation is mainly controlled by the SiOC composition and decreases as the amount of free carbon increases. However, MTES- and SR350-derived glasses show a different degree of phase separation, even though they have the same chemical composition, which suggests that other parameters may be important. Actually, it has already been reported in the literature that the molecular network structure of the preceramic precursor can be important in defining the final microstructure and properties of precursor-derived SiOC materials.<sup>34</sup>

The chemical-durability test data reported in Table II indicate that SiOC glasses are more durable than fused silica and soda-lime

**Table II. Results of Durability Tests Performed on SiOC Glasses**

Sample	In alkaline solution						In HF solution at 1200°C	
	Durability (mg <sub>SiO<sub>2</sub></sub> /g <sub>glass</sub> ) <sup>†</sup>			Durability (mg <sub>SiO<sub>2</sub></sub> /[m <sup>2</sup> (g <sub>Si</sub> + g <sub>O</sub> )/g <sub>glass</sub> ]) <sup>‡</sup>			Durability (mg <sub>SiO<sub>2</sub></sub> /g <sub>glass</sub> ) <sup>†</sup>	Durability (mg <sub>SiO<sub>2</sub></sub> /[m <sup>2</sup> (g <sub>Si</sub> + g <sub>O</sub> )/g <sub>glass</sub> ]) <sup>‡</sup>
	1000°C	1200°C	1400°C	1000°C	1200°C	1400°C		
T <sup>H</sup> /D <sup>H</sup> 2/1	50.0 ± 5	8.1 ± 0.8	12.0 ± 1.2	270 ± 81	29 ± 9	33 ± 10	3.5 ± 0.3	13 ± 3.8
MTES	16.8 ± 1.7	5.0 ± 0.5	5.7 ± 0.6	22 ± 7	16 ± 2	11 ± 3	3.3 ± 0.3	4 ± 1.2
SR350	2.9 ± 0.3	1.8 ± 0.2	5.0 ± 0.5	5 ± 1	3 ± 1	10 ± 3	0.4 ± 0.3	1 ± 0.3
SR355	6.0 ± 0.6	2.5 ± 0.2		12 ± 3	6 ± 2		1.4 ± 0.1	3 ± 0.9
SiO <sub>2</sub> (<1 ppm OH)		14.0 ± 1.4			70 ± 21		13.0 ± 1.3	65 ± 19.5
SiO <sub>2</sub> (700 ppm OH)		12.3 ± 1.2			62 ± 18		14.0 ± 1.4	70 ± 21
Soda-lime		13.5 ± 1.3			96 ± 29		113 ± 11.3	807 ± 242

<sup>†</sup>Error given as ±10%. <sup>‡</sup>Error given as ±30%.

glass, in both acidic (HF) and alkaline solutions. It is well-known that in alkaline solutions, OH<sup>-</sup> ions are able to break the strongly polarized Si—O—Si bonds of the silica network by a nucleophilic attack on the Si<sup>4(6+)</sup> atom, according to the reaction<sup>27,35</sup>



A similar mechanism of silica depolymerization also occurs when the glass is attacked by F<sup>-</sup> ions; in this case, the reaction is



The presence of carbon in the silica network results in the formation of Si—C bonds that, in comparison with the Si—O bonds, have less-ionic character. Thus, Si atoms that are engaged in Si—C bonds display a lower positive partial charge (δ<sup>+</sup>) and should be more stable toward nucleophilic attack by either OH<sup>-</sup> or F<sup>-</sup> ions. Indeed, SiC is not attacked by either alkaline or HF solutions.<sup>36</sup>

The XPS data obtained after the durability tests show a depletion of silica [SiO<sub>4</sub>] species and an enrichment of carbon. This result reveals an important effect of leaching on the surface. Namely, the Si atoms that are bonded to four O atoms (as in silica) are depleted (presumably they are the atoms that are carried away into solution); the corresponding depletion of surface O atoms after leaching is consistent with this observation. In addition, there is an accumulation of C atoms on the surface, presumably because no mechanism to solubilize them is present. An accumulation of the Si atoms that are bonded to one or more C atoms (Si<sup>1</sup>), in the case of T<sup>H</sup>/D<sup>H</sup> 2/1 and MTES, is also observed; however, no such accumulation is observed for the SR350 and SR355.

To explain these various effects of leaching on the surface chemical structure, and to relate the leaching behavior to the initial composition of glass, one must consider the chemical structure

(Si—C versus Si—O versus C—C bonds) as well as the microstructure (phase separation and three-dimensional (3-D) connectivity of SiOC versus SiO<sub>2</sub> versus free-carbon phases). Generally, the trend from T<sup>H</sup>/D<sup>H</sup> 2/1 to MTES to SR350 and SR355 is such that the glasses become less phase-separated and the amount of free carbon increases. We will discuss the influence of these two microstructural features separately:

(1) It seems reasonable to suppose that the more the glass is phase-separated into carbon, SiC, and SiO<sub>2</sub> (the equilibrium assemblage of phases), the easier it should be to leach out the SiO<sub>2</sub> phase. The relation of the higher the pyrolysis temperature, the more phase-separated the microstructure also is clear. On the other hand, in a homogeneous amorphous silicon oxycarbide glass, the Si—O and Si—C bonds are randomly distributed throughout the network. Moreover, Si atoms that are bonded to at least one C atom are not readily extracted by OH<sup>-</sup> or F<sup>-</sup> chemical attack. Thus, the Si—C bonds resist leaching and dissolution themselves; in addition, these Si—C bonds, if randomly distributed, can provide a chemical and physical impediment to the attack of the Si—O bonds in nearby silicate ([SiO<sub>4</sub>]) or silicon oxycarbide (SiC<sub>x</sub>O<sub>4-x</sub>, where x = 1, 2, 3) species.

(2) The role of the free-carbon phase is twofold. First, as shown from the XRD analysis and in agreement with the literature,<sup>4,29</sup> the free-carbon phase provides an interphase between SiC nanocrystallites and, thereby, can inhibit their growth; this condition has an effect on leaching, because it limits any decomposition of the SiOC phase to form the more-soluble SiO<sub>2</sub>. Second, free carbon is insoluble in alkaline or HF solutions; therefore, it will act as a chemical and physical barrier, hindering the attack or diffusion of OH<sup>-</sup> or F<sup>-</sup> ions at and within the surface. Indeed, Raman spectra recorded on the leached samples were very similar to those obtained for the initial unleached glasses (see Fig. 2). The Raman spectra still show the D and G bands with the initial intensity

**Table III. XPS Data on SiOC Samples Obtained at 1200°C<sup>†</sup>**

Leaching	Si <sup>1</sup>		Si <sup>2</sup>		Elemental content (at.%)	
	Content (at.%)	Binding energy (eV)	Content (at.%)	Binding energy (eV)	Carbon	Oxygen
			T <sup>H</sup> /D <sup>H</sup> 2/1			
Before	6.6	100.23	25.3	102.52	15.6	52.5
After	18.4	100.14	11.7	102.49	35.5	34.4
			MTES			
Before	6.0	100.43	19.3	102.35	29.5	45.2
After	9.5	99.94	8.4	102.39	53.7	28.4
			SR350			
Before	5.2	100.74	22.2	102.49	26.1	46.5
After	4.7	100.44	17.6	102.41	34.7	43.0
			SR355			
Before	1.9	100.86	14.6	102.73	46.2	37.3
After	0.2	100.65	2.6	101.95	73.7	23.5

<sup>†</sup>Si<sup>1</sup> denotes silicon in SiOC, and Si<sup>2</sup> denotes silicon in SiO<sub>2</sub>.

ratios. Carbon may also amass progressively on the surface (because of the dissolution of  $[\text{SiO}_4]$  species) and, thereby, provide an additional physical barrier between the glass and the solution.

According to the proposed chemical structure and microstructure (phase separation) of the SiOC glasses, the durability of the studied SiOC glasses pyrolyzed at 1200°C can be explained as follows.  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1, despite having the greatest amount of Si—C bonds, also has the most-phase-separated system and, for this reason, is also the least durable. MTES shows better alkaline durability ( $16 \pm 2 \text{ mg}_{\text{SiO}_2}/[\text{m}^2(\text{g}_{\text{Si}} + \text{g}_{\text{O}})/\text{g}_{\text{glass}}]$ ), compared to that registered for the  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1 ( $29 \pm 9 \text{ mg}_{\text{SiO}_2}/[\text{m}^2(\text{g}_{\text{Si}} + \text{g}_{\text{O}})/\text{g}_{\text{glass}}]$ ), because of its lower degree of phase separation. The role of phase separation can be evaluated more directly by comparing the results for MTES and SR350; indeed, these two glasses have the same composition, but MTES is phase-separated whereas SR350 is still a homogeneous glass (see Fig. 1). Accordingly, SR350 displays better durability than MTES. Similarly, the effect of carbon (independent of phase separation) can be evaluated by comparing the SR350- and SR355-derived glasses. The alkaline durability of SR355-derived glass is slightly lower than SR350-derived glass. The two glasses are both homogeneous and not phase separated; however, the SR355-derived glass contains fewer Si—C bonds, which may explain its slightly lesser chemical durability. The HF resistance of the SiOC glasses follows these same trends; e.g., the pure SiOC glass that was derived from  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1 was the least durable, and that derived from SR350 was the most resistant.

The influence of pyrolysis temperature on the chemical durability of SiOC glasses has been studied under the alkaline conditions. Let us first consider the role of the annealing temperature on the structure of SiOC glasses. The effect of the pyrolysis temperature is twofold. First, during the organic–inorganic conversion, the increase of the maximum temperature of the pyrolysis treatment leads to higher degree of conversion, which means a more cross-linked SiOC network with fewer terminal  $\text{CH}_2$  or  $\text{CH}$  groups. This stage is active up to a maximum temperature of  $\sim 1000^\circ\text{--}1200^\circ\text{C}$ . Second, by increasing the temperature to  $>1000^\circ\text{--}1200^\circ\text{C}$ , the homogeneous SiOC structure starts to phase-separate to SiC and  $\text{SiO}_2$ . The alkaline-release values measured for MTES-, SR350-, and SR355-derived SiOC glasses pyrolyzed at 1000°C are slightly higher than the corresponding data at 1200°C but are still lower than those in the reference systems. Such a result can be explained by considering the glass structure at 1000°C to be less cross-linked than that at 1200°C (because of the presence of residual hydrogen); thus, the 1000°C SiOC glasses are less durable. This finding is consistent with a similar result that has already been reported in the literature on the influence of the pyrolysis temperature on the oxidation resistance of SiOC glasses.<sup>37</sup> The rather-low alkaline resistance that has been

measured for the  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1 glass at 1000°C ( $270 \pm 81 \text{ mg}_{\text{SiO}_2}/[\text{m}^2(\text{g}_{\text{Si}} + \text{g}_{\text{O}})/\text{g}_{\text{glass}}]$ ) is due to two factors: (i) the (already mentioned) presence of residual hydrogen, which is responsible for a less cross-linked network, and (ii) the incipient phase separation, which (in this system) begins at  $\sim 1000^\circ\text{C}$ . The alkaline resistance from 1200°C to 1400°C shows rather-constant values for the  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1- and MTES-derived glasses, whereas for the SR350-derived glasses, the durability at 1400°C clearly decreases. These results are in good agreement with the microstructural evolution of these three systems:  $\text{T}^{\text{H}}/\text{D}^{\text{H}}$  2/1- and MTES-derived glasses are already phase-separated at 1200°C, and the increase of temperature up to 1400°C only leads to a slight increase of the  $\beta$ -SiC grain size; on the other hand, for SR350-derived glass, the transition from 1200°C to 1400°C transforms the homogeneous glassy network to a phase-separated network, with a subsequent decrease of the chemical durability. Finally, we compared the HF attack of SiOC and fused silica by examining the morphology of the glass surfaces before and after leaching. The SEM micrographs in Fig. 3 show that the fused-silica surface is uniformly covered with the typical etched polishing lines after HF attack, whereas the SiOC sample is still smooth. This result provides visual evidence of the greater chemical durability of the SiOC glass under these aggressive conditions. The AFM data in Fig. 4 provides additional evidence.

## V. Summary

The conclusions, for both alkaline and HF attack, are as follows:

- (1) The SiOC phase exhibits greater durability than the  $\text{SiO}_2$  phase, because of the character of the bonding (Si—C bonds are less prone to nucleophilic attack) and a higher degree of compositional disorder and crosslinking. (Carbon, either bonded to Si atoms or present as a free-carbon phase, impedes reactant transport locally.)
- (2) Phase separation (into  $\text{SiO}_2$ -based SiC and carbon regions) exerts a major influence on the durability of the system. The chemical durability increases as the amount of phase separation decreases, because the system generally becomes more similar to SiOC. As the amount of phase separation increases, the silica/silicate species can be extracted; the more “interconnected” the separated silica/silicate phase, the more readily this phenomenon occurs. The presence and extent of the phase separation is related to the composition of the starting precursor (increases as the C/Si ratio decreases) and the pyrolysis temperature (increases as the pyrolysis temperature increases). Other factors, such as the preceramic architecture, also may have some influence.

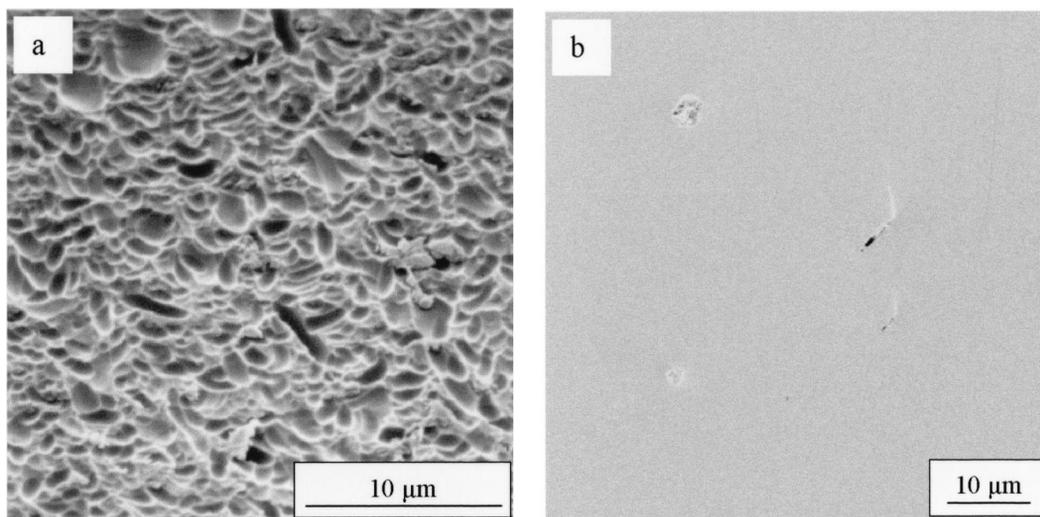


Fig. 3. SEM micrographs of the surface of glasses after HF attack ((a) MTES-derived SiOC glass, pyrolyzed at 1200°C, and (b)  $\text{SiO}_2$  glass ( $[\text{OH}] < 1 \text{ ppm}$ )).

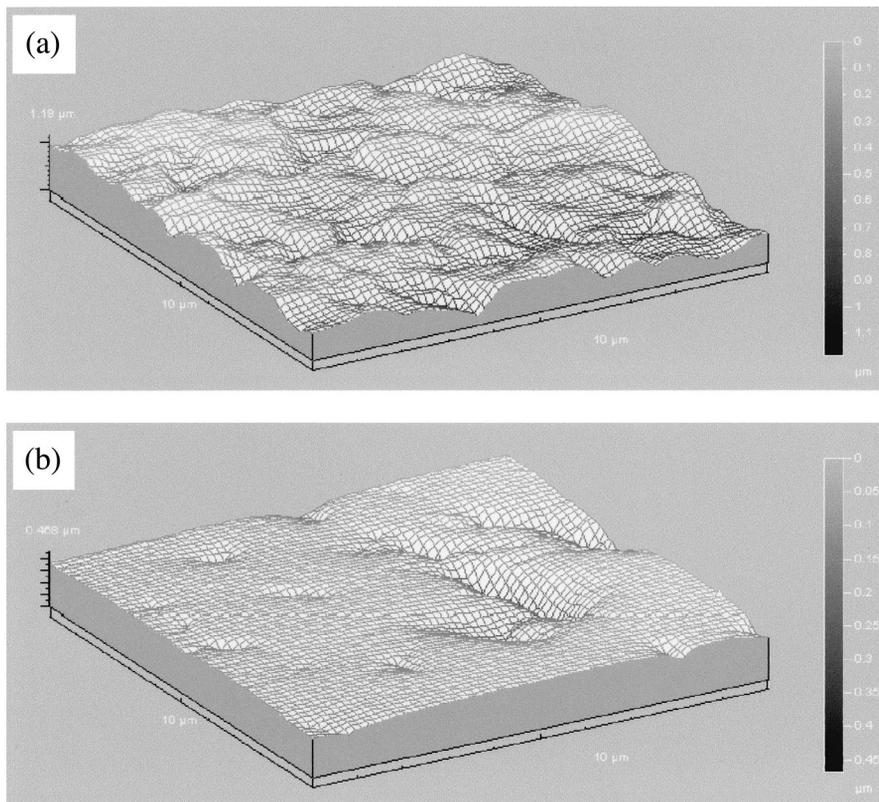


Fig. 4. AFM patterns of the surface of glasses after HF attack ((a) MTES-derived SiOC glass, pyrolyzed at 1200°C, and (b) SiO<sub>2</sub> glass ([OH] < 1 ppm).

(3) In this study, the alkaline and HF durability was greatest for the polymer-derived SiOC glasses (SR350 > SR355 > MTES > T<sup>H</sup>/D<sup>H</sup> 2/1).

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#### References

- R. Riedel, "Advanced Ceramics from Inorganic Polymers"; pp. 1–50 in Materials Science and Technology, A Comprehensive Treatment, Vol. 17B, *Processing of Ceramics, Part II*. Edited by R. J. Brook. VCH, Wurzburg, Germany, 1996.
- R. Riedel, L. M. Ruswisch, L. N. An, and R. Raj, "Amorphous Silicoboron Carbonitride Ceramic with Very High Viscosity at Temperatures above 1500°C," *J. Am. Ceram. Soc.*, **81**, 3341–44 (1998).
- R. Riedel, A. Kienzle, W. Dressler, L. Ruwisch, J. Bill, and F. Aldinger, "A Silicoboron Carbonitride Ceramic Stable to 2000°C," *Nature (London)*, **382**, 796–98 (1996).
- C. Turquat, H. J. Kleebe, G. Gregori, S. Walter, and G. D. Sorarù, "TEM and EELS Study of Non-Stoichiometric SiCO Glasses," *J. Am. Ceram. Soc.*, **84**, 2189–96 (2001).
- C. G. Pantano, A. K. Singh, and H. X. Zhang, "Silicon Oxycarbide Glasses," *J. Sol-Gel Sci. Technol.*, **14**, 7–25 (1999).
- (a) G. M. Renlund, S. Prochazka, and R. H. Doremus, "Silicon Oxycarbide Glasses: Part I. Preparation and Chemistry," *J. Mater. Res.*, **6**, 2716–22 (1991). (b) G. M. Renlund, S. Prochazka, and R. H. Doremus, "Silicon Oxycarbide Glasses: Part II. Structure and Properties," *J. Mater. Res.*, **6**, 2723–34 (1991).
- H. Zhang and C. G. Pantano, "Synthesis and Characterization of Silicon Oxycarbide Glasses," *J. Am. Ceram. Soc.*, **73**, 958–63 (1990).
- R. J. P. Corriu, D. Leclercq, P. H. Mutin, and A. Vioux, "Si-29 Nuclear-Magnetic-Resonance Study of the Structure of Silicon Oxycarbide Glasses Derived from Organosilicon Precursors," *J. Mater. Sci.*, **30**, 2313–18 (1995).
- L. Bois, J. Maquet, F. Babonneau, and D. Bahloul, "Structural Characterization of Sol-Gel Derived Oxycarbide Glasses. 2, Study of The Thermal-Stability of the Silicon Oxycarbide Phase," *Chem. Mater.*, **7**, 975–81 (1995).
- F. Babonneau, G. D. Sorarù, G. D'Andrea, S. Dirè, and L. Bois, "Silicon-Oxycarbide Glasses from Sol-Gel Precursors," *Mater. Res. Soc. Symp. Proc.*, **271**, 789–94 (1992).
- G. 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).
- J.-H. Kleebe, C. Turquat, and G. D. Sorarù, "Phase Separation in a SiCO Glass Studied by Transmission Electron Microscopy and Electron Energy-Loss Spectroscopy," *J. Am. Ceram. Soc.*, **84**, 1073–80 (2001).
- R. E. Loehman, "Oxynitride Glasses"; pp. 119–49 in *Treatise on Materials Science and Technology*, Vol. 26, *Glass IV*. Edited by M. Tomozawa and R. H. Doremus. Academic Press, New York, 1985.
- G. H. Frischat and K. Sebastian, "Leach Resistance of Nitrogen-Containing Na<sub>2</sub>O-CaO-SiO<sub>2</sub> Glasses," *J. Am. Ceram. Soc.*, **68**, C-305–C-307 (1985).
- K. Kamiya, M. Ohya, and T. Yoko, "Nitrogen-Containing SiO<sub>2</sub> Glass Fibers Prepared by Ammonolysis of Gels Made from Silicon Alkoxides," *J. Non-Cryst. Solids*, **83**, 208–22 (1986).
- G. D. Sorarù, E. Dallapiccola, and G. D'Andrea, "Mechanical Characterization of Sol-Gel-Derived Silicon Oxycarbide Glasses," *J. Am. Ceram. Soc.*, **79**, 2074–80 (1996).
- N. Suyal, T. Krajewski, and M. Mennig, "Sol-Gel Synthesis and Microstructural Characterization of Silicon Oxycarbide Glass Sheets with High Fracture Strength and High Modulus," *J. Sol-Gel Sci. Technol.*, **13**, 995–99 (1998).
- M. Hammod, E. Breval, and C. G. Pantano, "Microstructure and Viscosity of Hot Pressed Silicon Oxycarbide Glasses," *Ceram. Eng. Sci. Proc.*, **14**, 947–54 (1993).
- T. Rouxel, G. Massouras, and G. D. Sorarù, "High Temperature Behavior of an SiOC Oxycarbide Glass: Elasticity and Viscosity," *J. Sol-Gel Sci. Technol.*, **14**, 83–94 (1999).
- G. D. Sorarù and D. Suttor, "High Temperature Stability Of Sol-Gel-Derived SiOC Glasses," *J. Sol-Gel Sci. Technol.*, **14**, 69–74 (1999).
- C. M. Brewer, D. R. Bujalski, V. E. Parent, K. Su, and G. A. Zank, "Insights into the Oxidation Chemistry of SiOC Ceramics Derived from Silsesquioxanes," *J. Sol-Gel Sci. Technol.*, **14**, 49–68 (1999).
- N. Suyal, T. Krajewski, and M. Mennig, "Microstructural and Dielectric Characterization of Sol-Gel Derived Silicon Oxycarbide Glass Sheets," *J. Sol-Gel Sci. Technol.*, **14**, 113–23 (1999).
- J. Cordelair and P. Greil, "Electrical Conductivity Measurements as a Microprobe for Structure Transitions in Polysiloxane Derived Si-O-C Ceramics," *J. Eur. Ceram. Soc.*, **20** [12] 1947–57 (2000).
- A. M. Wilson, G. Zank, K. Eguchi, W. Xing, B. Yates, and J. R. Dahn, "Pore Creation in Silicon Oxycarbides by Rinsing in Dilute Hydrofluoric Acid," *Chem. Mater.*, **9**, 2139–44 (1997).
- S. R. Song, "Chemical Vapor Deposition of Silicon Oxycarbide Thin Films by Oxy-Carbonization of SiH<sub>4</sub>-CO<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> Mixtures"; Ph.D. Dissertation. Pennsylvania State University, University Park, PA, 1999.
- M. Egan and C. G. Pantano, "Chemical Structure of Silicon Oxycarbide Glasses by XPS," *Surf. Int. Anal.*, 2001.
- R. K. Iler, *The Chemistry of Silica*. Wiley, New York, 1979.
- L. Bois, J. Maquet, F. Babonneau, H. Mutin, and D. Bahloul, "Structural Characterization of Sol-Gel Derived Oxycarbide Glasses, I—Study of the Pyrolysis Process," *Chem. Mater.*, **6**, 796–802 (1994).
- M. Monthieux and O. Delverdiere, "Thermal Behavior of (Organosilicon) Polymer-Derived Ceramics, V: Main Facts and Trends," *J. Eur. Ceram. Soc.*, **16**, 721–37 (1996).

<sup>30</sup>S. Modena, "Proprietà Chimiche dei Vetri Ossicarburi"; Tesi di laurea in Ingegneria dei Materiali. Università di Trento, Trento, Italy, 2000.

<sup>31</sup>Y. Yang, D. C. Alsmeyer, and R. L. McCreery, "Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra," *Chem. Mater.*, **2**, 557–63 (1990).

<sup>32</sup>F. Tuinstra and L. L. Koenig, "Raman Spectrum of Graphite," *J. Chem. Phys.*, **53**, 1126–30 (1970).

<sup>33</sup>G. D. Sorarù, G. D'Andrea, R. Campostrini, F. Babonneau, and G. Mariotto, "Structural Characterization and High Temperature Behaviour of Silicon Oxycarbide Glasses Prepared from Sol-Gel Precursors Containing Si-H Bonds," *J. Am. Ceram. Soc.*, **78**, 379–87 (1995).

<sup>34</sup>G. D. Sorarù, Q. Liu, L. V. Interrante, and T. Apple, "The Role of Precursor Molecular Structure on the Microstructure and High Temperature Stability of Silicon Oxycarbide Glasses Derived from Methylene-Bridged Polycarbosilanes," *Chem. Mater.*, **10**, 4047–54 (1998).

<sup>35</sup>A. Paul, *Chemistry of Glasses*, 2nd Ed.; pp. 186–87. Chapman and Hall, London, U.K., 1995.

<sup>36</sup>K. G. Nickel and Y. G. Gogotsi, "Corrosion of Hard Materials"; pp. 140–77 in *Handbook of Ceramic Hard Materials*. Edited by R. Riedel. Wiley-VCH, Weinheim, Germany, 2000.

<sup>37</sup>H. Zhang and C. G. Pantano, "High Temperature Stability of Oxycarbide Glasses," *Mater. Res. Soc. Symp. Proc.*, **271**, 783–88 (1992). □