

Thermal Redistribution Reactions of Blackglas™ Ceramic

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ABSTRACT: Silicon oxycarbides undergo Si—O and Si—C bond redistribution when heated in an inert atmosphere above 900°C. This redistribution has a great influence on the mechanical, thermal, and oxidative stability properties of Blackglas™ ceramic. Based on a statistical method, three independent thermal redistribution reactions were chosen to describe the redistribution reactions between 900 and 1350°C. Over this temperature range, only Si—O and Si—C bond redistribution is involved, and the char yield is constant. The equilibrium constants of each independent reaction and their temperature dependence are calculated directly by using ²⁹Si-NMR experimental data for temperatures of 900, 1000, and 1100°C and fitted to a cubic polynomial. A redistribution reaction model (RRM) is proposed to describe how the microcompositions of silicon oxycarbide change with respect to temperature. The model is based on ²⁹Si-NMR data from 900 to 1100°C. It enables one to extrapolate results to 1400°C and indicates that the silicon oxycarbide can survive above 1400°C and that the microcomposition is very sensitive to the ratio O/Si in the polymer precursor. This prediction is in a good agreement with the experimental results observed by Belot et al., Corriu et al., Bois et al., and F. Babonneau et al. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 143–152, 2001

Key words: silicon oxycarbides; Blackglas™; NMR; redistribution reactions; pyrolysis; Nicalon; oxidative stability; mechanical/thermal properties

INTRODUCTION

Silicon oxycarbide ($\text{SiC}_x\text{O}_{2(1-x)}$), a refractory glass, is a random network of silicon–oxygen tetrahedra, where some divalent oxygen atoms are substituted for the tetravalent carbon atoms. The mechanical, thermal, and chemical properties of silicon oxycarbide glass are superior to those of silica glass.^{1–3} This improvement is directly pro-

portional to the amount of carbon that is incorporated into the network of silica glass. The melting of a silica-based glass in the presence of silicon carbide leads to the incorporation of carbon as low as 0.5 wt %, because of the reduction reaction between silicon carbide and silica at high temperature. However, a high level of carbons can be incorporated at the atomic scale by the pyrolysis of polysiloxane (R_2SiO) at a temperature below 1200°C. During the transformation, as illustrated in Figure 1, small hydrocarbons like methane and hydrogen are evolved. Free carbons are usually formed above 600°C and are uniformly embedded in the silicon oxycarbide phase. Due to the color of free carbon, the glasses formed are also called black glasses.^{1,4–8} The relative ease of introducing carbon as Si—C bonds into the structure of

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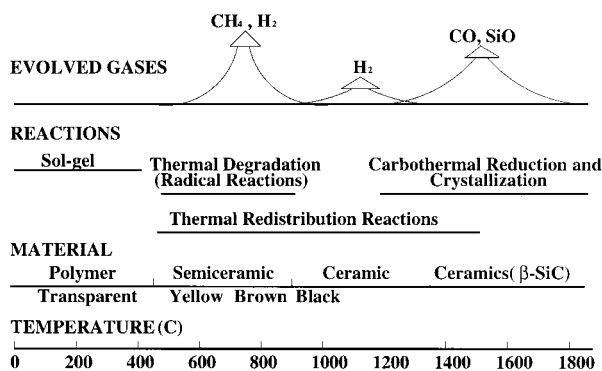


Figure 1 Transformation of polymer to ceramic.

preceramic polymers and the relatively low temperatures required to convert preceramic polymers into black glasses make them a good candidate for the matrix material of composites.^{6–11} Blackglas™ ceramic, invented by Leung,⁴ is an excellent candidate for use as a composite that operates in the 260–1200°C regime, such as a component of a gas-turbine engine.

As illustrated in Figure 1, in addition to the radical reactions, redistribution reactions also occur between Si—H and Si—O bonds, Si—C and Si—O bonds, and Si—O and Si—O bonds.^{12–15} These redistribution reactions are equilibrium reactions in which two substituents on two central Si atoms are exchanged, for instance,



The exchange of Si—H/Si—O bonds takes place at a temperature as low as 300°C, whereas the exchange of Si—C and Si—O takes place above 500°C.¹⁵ The redistribution reactions between Si—H and Si—O bonds and Si—O and Si—O—bonds usually lead to chain fragmentation and the loss of small organosilicon molecules, which is detrimental both to the yield and to the homogeneity of the glass formed. For the formation of good materials, these reactions should be minimized. The redistribution reaction between Si—C and Si—O does not lead to the loss of small organosilicon molecules, but results in inhomogeneous glass. When heated at a temperature of 900–1350°C, the silicon oxycarbide phase is known to undergo redistribution reactions with a constant char yield.^{5,13–27} The thermal redistribution reactions change the microstructure of black glass, which affects the mechanical, thermal, and oxidative properties.

Nuclear magnetic resonance (NMR) is one of the most powerful aids in the study of redistribution reactions, because the chemical shift is sensitive to the atoms connectivity. This allows a monitoring of redistribution in the material. The ²⁹Si-NMR results show that the microstructure of black glass at 900°C depends on the ratio of O/Si in the preceramic polymer.^{12,13} Therefore, appropriate control of the thermal treatment temperature protocol and of the ratio of O/Si in the preceramic polymers are needed to obtain black glasses with the desired properties for a particular application.

As stated previously, the microstructure of silicon oxycarbide can be changed by varying the O/Si ratio in the preceramic polymers or the final pyrolysis temperature or both. Therefore, one can fabricate Blackglas™ ceramic with the desired properties by controlling the O/Si ratio in the preceramic polymers and the final pyrolysis temperature. The synthesis of preceramic polymers and the pyrolysis processing procedures for Blackglas™ composites have been developed by a costly, time-consuming, trial-and-error approach to achieve a ceramic with desired properties. The purpose of this article was to develop a redistribution reaction model (RRM), which can be used to predict how the microstructure of Blackglas™ ceramic changes with respect to temperature and to the O/Si ratio in the preceramic polymers. This information should be useful for designing the preceramic polymer and for understanding how the mechanical, thermal, and oxidative properties of Blackglas™ ceramic are related to the temperature protocol used in pyrolysis.

EXPERIMENTAL

The ²⁹Si-NMR experiments and data used here were published by Meador et al.²³ The experimental procedure was as follows: The samples were made with Blackglas™ 493A resin with 2% 493B catalyst added. Each sample was cured at 55°C for 3 h and postcured at 150°C for 2 h. After curing, each sample was pyrolyzed separately in high alumina boats in a 3-in. mullite tube furnace with a nitrogen flow of 2 L/min. The temperature protocol for the pyrolysis cycles involved a heating rate of 2°C/min up to the final pyrolysis temperature of 900, 1000, and 1100°C. The samples were held at one of these temperatures for 1, 3, and 5 h. All the samples lost approximately 18% of their mass by gas evolution during the pyrolysis cycle.

Table I Concentrations of Si Units with Respect to Temperature

Reference	O/Si	Temperature (°C)	SiC ₄ (%)	SiC ₃ O (%)	SiC ₂ O ₂ (%)	SiCO ₃ (%)	SiO ₄ (%)
23	1.06	900	23.65	2.50	32.00	27.50	14.35
		1000	30.40	1.80	24.60	24.40	18.80
		1100	35.31	1.40	16.50	21.45	25.34

The ²⁹Si-NMR experiments were performed using a Bruker AM-300 spectrometer, and the spectrometer was controlled by a TECMAG data system running MACNMR 5.1 software. The solid samples were run with magic-angle spinning at 5 kHz, and the spectra were referenced to the ²⁹Si peak of the sodium salt of 3-trimethylsilylpropionic acid (0 ppm). The ²⁹Si-NMR experimental results obtained are listed in Table I.

RANDOM DISTRIBUTION MODEL

By definition, a distribution reaction is one in which bonds change in a relative position but not in type according to Lockhart.²⁸ Suppose that a central atom *M* has a functionality of *n* and is connected to *m* different ligands *X*, *Y*, *Z*, . . . , *J* in the ceramic. Then, its microconstituents based on a central atom *M*, which in this case is silicon at equilibrium, can be considered statistically to be a mixture of random distributed compounds with the formula $MX_aY_bZ_c \dots J_j$, where *a*, *b*, *c*, . . . , *j* are the numbers of atoms *X*, *Y*, *Z*, . . . , *J* connected to the central atom *M*, respectively. The sum of *a*, *b*, *c*, . . . , *j* is equal to the number of the functionality of the central atom *M*, that is, $a + b + c + \dots + j = n$. The number of different compounds which can be formed is

$$\frac{(n + m - 1)!}{n!(m - 1)!}$$

Let the mol fractions of the *X* groups be f_x ; of the *Y* groups, f_y ; of the *Z* groups, f_z ; . . . , of *J* groups, f_j relative to the central atom *M*. Then, the concentration of the mixed compound $MX_aY_bZ_c \dots J_j$ is

$$\frac{n!}{a!b!c! \dots j!} f_x^a f_y^b f_z^c \dots f_j^j$$

where $f_x + f_y + f_z + \dots + f_j = 1$.

For a silicon oxycarbide phase, silicon with a functionality of 4 ($n = 4$) is taken as the central atom because ²⁹Si-NMR is used to study redistribution reactions. According to elemental analysis, the black glass ceramic consists only of silicon, carbon, and oxygen. Therefore, the ligands of silicon are carbon and oxygen ($m = 2$). Statistically, the number of different compounds which can be formed is

$$\frac{(4 + 2 - 1)!}{4!(2 - 1)!} = 5$$

which are SiC₄, SiC₃O, SiC₂O₂, SiCO₃, and SiO₄.

In black glass, all oxygen atoms exist in the form of Si—O—Si bridges, and the silicon atoms are bonded to carbon and oxygen atoms only, as confirmed by the ²⁹Si-MAS-NMR and XPS results.^{1,11} Based on the above facts, Corriu et al.²⁵ proposed that the silicon oxycarbide species would be a random distribution of Si—O and Si—C bonds with the concentration of SiO_{*x*}C_{4-*x*} given by

$$\frac{4!}{x!(4-x)!} f_{\text{olsi}}^x f_{\text{clsi}}^{4-x}$$

The probability of finding a Si—O bond depends on the mol ratio of O/Si in the black glass and is given by

$$f_{\text{olsi}} = \frac{r}{2}$$

$$f_{\text{clsi}} = 1 - f_{\text{olsi}}$$

where *r* is the mol ratio of O/Si in the black glass. For two preceramic polymers with the O/Si ratios of 1.2 and 1.7, Corriu et al.²⁵ compared the concentrations of SiO_{*x*}C_{4-*x*} calculated from their random model with the ²⁹Si-NMR results of black glasses pyrolyzed at 10°C/min to 900°C and an-

Table II Comparison Between Random Model and Experiments

Site	Random Model (%)	Experiment ²³ (%)
SiC ₄	4.88	23.65
SiC ₃ O	22.01	2.5
SiC ₂ O ₂	37.23	32.00
SiCO ₃	27.99	27.50
SiO ₄	7.89	14.35

nealed for 30 min and reasonable agreement was obtained.

For Blackglas™ ceramic, the atomic formula is SiC_{1.209}O_{1.06} based on the element analysis. The calculated concentrations of Si sites from the random model and experiment are illustrated in Table II.

There is no sound theoretical basis to support the assumption that the silicon oxycarbide reaches a random distribution at 900°C, and the data²³ shown in Table II do not agree well with this model. The effect of temperature is also not included in the random distribution model of Corriu et al.²⁵ Consequently, the relative concentrations of SiO_xC_{4-x} of black glass pyrolyzed at a temperature above 900°C cannot be predicted. Hurwitz,²² Babonneau,¹⁹ and Belot et al.¹⁸ confirmed that the relative concentrations of SiO_xC_{4-x} change with the final pyrolysis temperature.

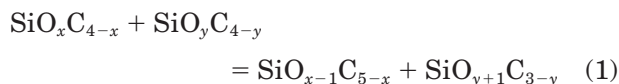
Compared to redistribution reactions in the liquid state, the redistribution reactions in the solid black glass are expected to be very slow due to transport limitations, and they do not reach equilibrium until about 1 h of holding time, as indicated by Zhang.²⁹ As a result, in the experiment of Corriu et al.,²⁵ the 30-min annealing time is not enough for the black glass pyrolyzed at 900°C to reach thermal equilibrium. In fact, the appearance of SiC₄ (*X*), SiC₃O (*M*), SiC₂O₂ (*D*), SiCO₃ (*T*), and SiO₄ (*Q*) sites in black glass, and the change of their relative concentrations with respect to temperature, as shown in Table I, strongly indicate that the silicon oxycarbide phase is determined by the thermal redistribution reactions which are a function of temperature.

THERMAL REDISTRIBUTION REACTIONS

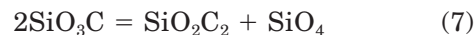
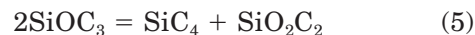
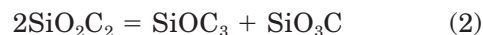
As confirmed by ²⁹Si-NMR of black glass heated at a temperature above 900°C,^{22,23} the redistribu-

tion reactions between Si—C and Si—O bonds lead to domains rich in Si—O bonds and domains rich in Si—C bonds with a constant char yield in a temperature range of 900–1350°C. The free carbon phase, formed during the polymer transformation to ceramic above 600°C, is still present as revealed from a comparison between the ²⁹Si-NMR data and chemical analysis.^{18,19} The percentage of carbon does not change over the temperature range of 900–1350°C. Therefore, it is reasonable for us to assume that the free carbon phase does not have a significant effect on the redistribution reactions of the silicon oxycarbide phase.

The preceramic polymers are totally transformed into black glass ceramic at 900°C, as indicated by TGA–RGA and chemical analysis of the elements. The formation of the silicon atom environment can be accounted for by the continuation of redistribution reactions of Si—C and Si—O bonds. These redistribution reactions ultimately lead to a random environment of the silicon atoms by the following exchange in which oxygen is lost and carbon is gained by one of the moieties while the reverse occurs in the other¹⁹:



where *x* and *y* are integers, 0 < *x* ≤ 4, and 0 ≤ *y* < 4. Based on eq. (1), the number of possible thermal redistribution reactions is six. The six possible thermal redistribution reactions occurring between 900 and 1350°C are shown as follows:



Independent Thermal Redistribution Reactions

As discussed in the previous section, there are six possible thermal redistribution reactions in the silicon oxycarbide phase, but some of the reactions can be generated by a combination of the

Table III Coefficients of Polynomial Fit for the Independent Reactions

Reaction	a_0	a_1	a_2	a_3
(2)	-6.1	2.0×10^{-2}	-2.2×10^{-5}	8.0×10^{-9}
(3)	-9.6×10^2	3.0	-3.2×10^{-3}	1.2×10^{-6}
(4)	-7.3	2.3×10^{-2}	-2.4×10^{-5}	8.6×10^{-9}

others by addition and subtraction, so only the independent reactions are needed to describe the redistribution between Si—O and Si—C bonds in the silicon oxycarbide phase. The number of independent reactions can be determined by statistical analysis.

Statistical Analysis

As indicated by the ^{29}Si -NMR and XPS results of black glass, there are five possible types ($\text{SiC}_x\text{O}_{4-x}$, $0 \leq x \leq 4$) in the silicon oxycarbide phase. The sum of the relative percentages of all five Si sites is equal to 1. If the relative percentages of any four Si types are known, the silicon oxycarbide phase can be described. From the thermal redistribution reactions (2)–(7), one knows that any two Si sites react with each other to generate another two Si sites, and that is also true for the reverse reaction. Therefore, the number of combinations of taking four elements two at a time is

$$C_4^2 = \frac{4 \times 3}{2} = 6$$

However, considering the fact that the reverse reaction enables any combination to be reactants or products, the number of independent reactions needed is $6/2 = 3$ to describe the redistribution between Si—O and Si—C bonds in the silicon oxycarbide phase.

Thermal Equilibrium Constants

Based on the ^{29}Si -NMR results for the polymer precursor postcured at 150°C , the SiO_2C_2 site is the dominant site. Therefore, the three independent thermal redistribution reactions that are used to describe the change of compositions of silicon oxycarbide are eqs. (2), (3) and (4), all of which involve SiO_2C_2 as a reactant. Because there is no thermodynamic data available for the compounds of SiOC_3 , SiO_2C_2 , and SiO_3C , one cannot calculate the thermal equilibrium constants based on the Gibbs–Helmholtz equation. How-

ever, the equilibrium constants for reactions (2), (3) and (4) can be calculated using the ^{29}Si -NMR results from Meador et al., shown in Table (I),²³ which gives the composition of the five components as a function of temperature and, therefore, of $K(T)$ for the range 900 – 1100°C . Since the reactions given by eqs. (2)–(7) proceed rapidly to completion, the equilibrium constants depend only on the holding temperatures which are 900 , 1000 , and 1100°C .

The calculated equilibrium constants for reactions (2), (3), and (4) with respect to temperature are fitted to a polynomial of order 3 by the subroutine E02ACF in the NAG library. The general formula for the equilibrium constant of an independent redistribution reaction with respect to temperature is of the form

$$K = a_0 + a_1 \times T + a_2 \times T^2 + a_3 \times T^3 \quad (8)$$

where a_0 , a_1 , a_2 , and a_3 are the coefficients of polynomial fit, and T , temperature ($^\circ\text{C}$). The coefficients of the polynomial fit for each independent distribution reactions are listed in Table III.

REDISTRIBUTION REACTION MODEL (RRM)

Black glass consists of a silicon oxycarbide and free carbon. When heated over the temperature range of 900 – 1500°C in a nitrogen atmosphere, the mass balance based on the ^{29}Si -NMR data and elemental analysis of silicon, carbon, and oxygen indicates that the free carbon remains constant.²¹ There is no carbothermal reduction reaction except thermal redistribution reactions. The residual hydrogen exists in the form of the C—H bond. The assumptions suggested by these facts and used in the development of model are

1. The free carbon is not involved in any redistribution reaction between Si—C and Si—O bonds.

2. The residual hydrogen only exists in the free carbon phase.

There are five unknown variables in the independent thermal redistribution reactions (2), (3), and (4). Suppose that C_1 , C_2 , C_3 , C_4 , and C_5 are the relative percentage of SiOC_3 , SiO_2C_2 , SiOC_3 , SiO_4 , and SiC_4 sites, respectively. Furthermore, let K_2 , K_3 , and K_4 be the equilibrium constants of eqs. (2), (3), and (4), respectively. To solve for five unknown variables, an additional two equations are needed in addition to three equations from the definition of K_2 , K_3 , and K_4 , and these constraints are provided by noting that

- The O/Si atomic ratio in Blackglas™ ceramic is the same as that in the preceramic polymer.
- The sum of the relative percentages of the five Si sites is equal to 1.

Then, the following equations are obtained from the definition of the equilibrium constant and the two constraints indicated above:

$$K_2 = \frac{C_1 \times C_3}{C_2^2} \quad (9)$$

$$K_3 = \frac{C_5 \times C_3}{C_2 \times C_1} \quad (10)$$

$$K_4 = \frac{C_1 \times C_4}{C_2 \times C_3} \quad (11)$$

$$C_1 + C_2 + C_3 + C_4 + C_5 = 1 \quad (12)$$

$$C_1 + 2 \times C_2 + 3 \times C_3 + 4 \times C_4 = A \quad (13)$$

where A is the O/Si ratio calculated based on the ^{29}Si -NMR data. Equation (13) derives from the fact that silicon and oxygen remain in the transformation of polymer to ceramic. There is one Si—O bond in SiOC_3 , two Si—O bonds in SiO_2C_2 , three Si—O bonds in SiO_3C , four Si—O bonds in SiO_4 , and zero Si—O bonds in SiC_4 . Thus, A is the sum of C_1 , two times C_2 , three times C_3 , four times C_4 , and zero times C_5 , as shown in eq. (13). The oxygen in the preceramic polymer and ceramic exists in the form of Si—O—Si. However, the O/Si ratio given by using ^{29}Si -NMR data does not consider this fact. Therefore, it should be a factor two of the O/Si mol ratio in the preceramic polymer, and A is equal to two times the O/Si mol ratio in the preceramic polymer.

The subroutine C05NBF in the NAG library is used to solve eqs. (9)–(13), which constitutes the RRM, for C_i ($i = 1$ –5). K_j ($j = 1$ –3) is given in the form of eq. (8); the coefficients in eq. (8) for K_j are listed in Table III.

RESULTS AND DISCUSSION

The calculated relative percentages of all Si sites for Blackglas™ ceramic pyrolyzed to 1000°C under nitrogen are shown in Figure 2 and are compared with experimental results. The agreement is considered to be satisfactory.

Because the experimental data²³ of ^{29}Si -NMR of Blackglas™ ceramic are limited to 900–1100°C, the equilibrium constants of eqs. (2), (3), and (4) are obtained only for this temperature range. However, eq. (8) enables one to extrapolate the data beyond this range. Only Si—C and Si—O bond redistribution reactions are involved in the temperature range of 900–1350°C, which was indicated by the ^{29}Si -NMR results of black glass.²¹ Therefore, we can use this RRM to predict the relative percentages of Si sites for extended temperature range from 1100 to 1350°C, and the predicted percentages of Si sites for temperatures 1200 and 1300°C are shown in Figure 3. As the final pyrolysis temperature increases, the relative percentages of SiOC_3 (M), SiO_2C_2 , and SiO_3C (T) sites decreases, whereas the percentages of SiO_4 (Q) and SiC_4 (X) sites increase, indicating that an increase of final pyrolysis temperature will lead to the domains rich in the Si—C bond and domains rich in the Si—O bond. At 1300°C, the relative percentages of SiO_4 and SiC_4 are about 40% each of the total Si sites, respectively, which is in agreement with experimental observations.^{20,27} The silicon oxycarbide phase may survive above 1400°C, as shown in Figure 4. This phase diagram was constructed by solving eqs. (9)–(13) for C_i ($i = 1$ –5) with an O/Si ratio of 1.06 for a temperature range from 900 to 1400°C.

The SiC_4 (X) tetrahedra structure is more compact than is the SiO_4 (Q) tetrahedra structure. Therefore, the more of the SiC_4 (X) site that is in Blackglas™ ceramic, the denser it is and the higher will be its oxidative stability,²¹ because oxygen diffusivity becomes smaller as Blackglas™ becomes denser. However, the oxidative stability of Blackglas™ ceramic is also closely related to the amounts of the free carbons in it. When the free carbon content reaches a threshold, the tiny carbon particles form continuous

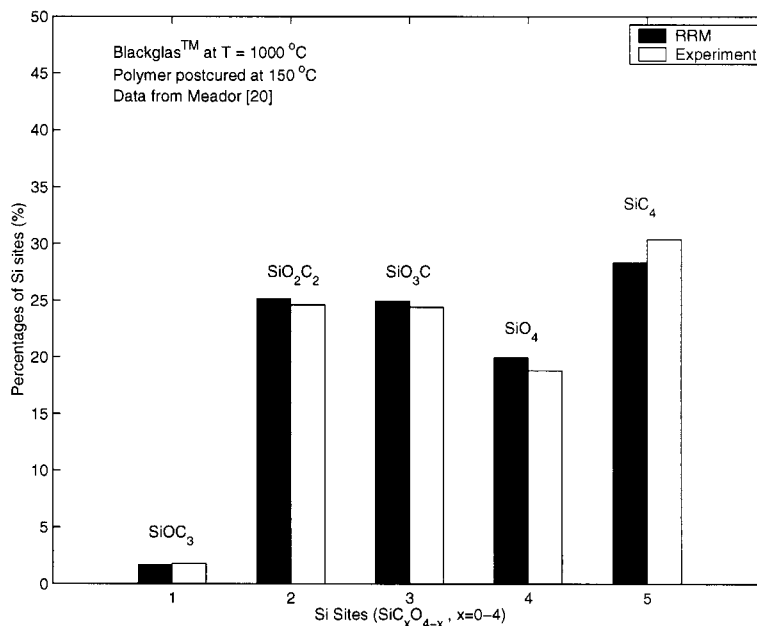


Figure 2 Comparison between RRM and ²⁹Si-NMR results of Blackglas™ ceramic at 1000°C.

paths through the ceramic and the oxidative stability of ceramic is lost.

In the transformation of polysiloxane to Blackglas™ ceramic, the silicon and oxygen are retained, as indicated by elemental analysis of pre-ceramic polymer, semiceramic, and ceramic,³⁰

and the oxygen exists in the form of Si—O—Si. Thus, the ratio of O/Si in the polymer precursors determines the composition of ceramic at 900°C. As shown in Figure 5, the ratio of O/Si in the polymer precursors changes the predicted composition of Blackglas™ ceramic at 900°C, and these predic-

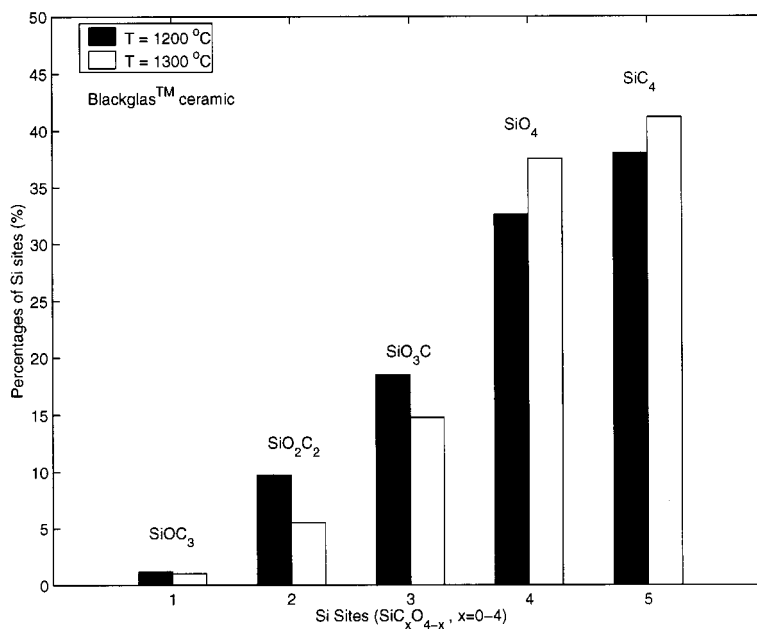


Figure 3 Percentages of Si sites of Blackglas™ ceramic at 1200 and 1300°C predicted by the RRM.

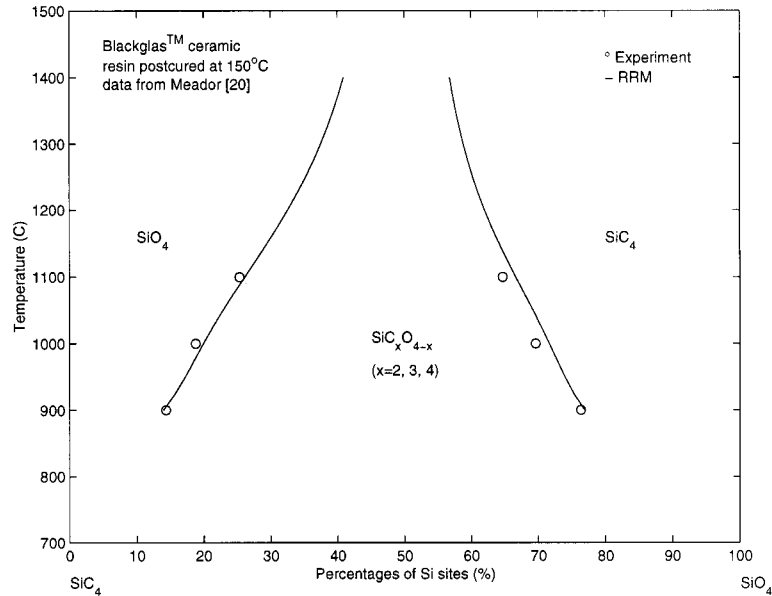


Figure 4 Phase diagram of silicon oxycarbide in Blackglas™ ceramic.

tions are in a good agreement with experimental observation.^{6,25,26} The percentages of SiO_4 (Q) and SiC_4 (X) sites are very sensitive to the change of the ratio O/Si . Therefore, it is possible to reengineer the polymer precursors to obtain the ceramic with the desired thermal and mechanical properties.

APPLICATIONS OF RRM TO OTHER MATERIALS

This RRM can be used to predict the relative percentages of Si sites of the silicon oxycarbide phase in

other black glass produced from different preceramic polymers^{24,31} and in Nicalon.³² Renlund³² characterized Nicalon fiber by both elemental analysis and ^{29}Si -MAS-NMR. Using the O/Si ratio from elemental analysis of Nicalon fiber and a final pyrolysis temperature 1200°C , the relative percentages of Si sites of the Nicalon fiber predicted by RRM are in a good agreement with those from the ^{29}Si -MAS-NMR experiments, as illustrated in Figure 6.

Shi³¹ pyrolyzed the polymer precursor of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane (CBS)

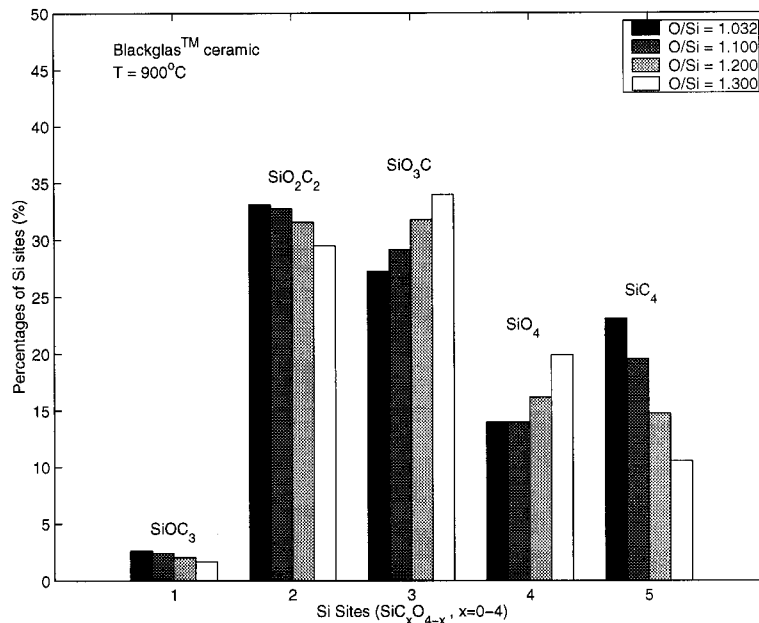


Figure 5 Effects of O/Si ratio on silicon oxycarbide phase in Blackglas™ ceramic predicted by RRM.

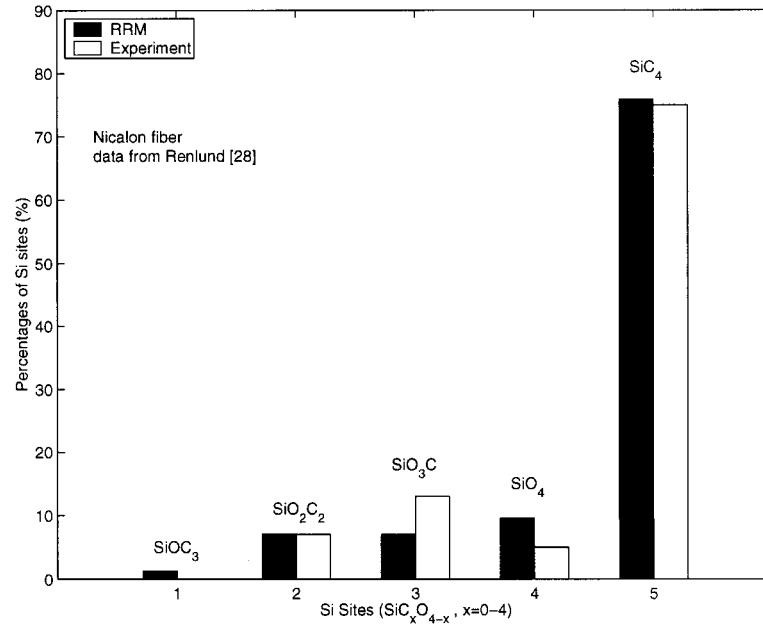


Figure 6 Comparison between RRM and ^{29}Si -NMR results of Nicalon fiber.

to 1000°C in nitrogen at a heating rate of 5°C/min. The relative percentages of Si sites of silicon oxycarbide from ^{29}Si -NMR experiments and our RRM are illustrated in Table IV. The black glass from the methylsilsesquioxane (MSQ) precursor also was characterized by ^{29}Si -SSNMR. The relative percentage of Si sites of silicon oxycarbide from the ^{29}Si -SSNMR experiments were compared again with those calculated from RRM, as shown in Table IV.

Corriu et al.²⁴ characterized the silicon oxycarbides pyrolyzed at 900°C from polymer precursors [crosslinked oligovinylsiloxane (COVS, $\text{SiO}_{1.14}\text{C}_{1.74}$) and crosslinked polyethylene (CPSE, $\text{SiO}_{1.29}\text{C}_{1.41}$)].¹⁵ The calculated relative percentages of Si sites of silicon oxycarbides from COVS and CPSE are

compared with their corresponding experimental results, as shown in Table IV. The percentage of the SiOC_3 (M) site predicted by the model is lower than the experimental result, whereas the percentage of the SiC_4 (X) site predicted by model is higher. The short annealing time (30 min) may contribute to the deviation of experimental result from the model prediction because the thermal redistribution reactions are slow in the solid silicon oxycarbide phase.²⁹ The overlapped ^{29}Si -NMR peaks of SiC_4 (X) and SiOC_3 (M) sites may be another factor in causing the difference between the model and experimental results.

In summary, no matter what kind of polymer precursor one uses, the microstructure of silicon oxycarbide is solely determined by the O/Si ratio

Table IV Comparison Between Experiments^{24,31} and RRM

Precursor	Temperature (°C)		Si Sites (%)				
			SiC ₄	SiC ₃ O	SiC ₂ O ₂	SiCO ₃	SiO ₄
CBS ³¹	1000	Exp.	2.0	23.0	38.3	29.1	7.6
		RRM	1.0	21.22	30.97	35.41	11.40
MSQ ³¹	1000	Exp.	0.68	17.61	31.44	43.95	6.33
		RRM	0.00	18.4	37.6	39.1	5.0
COVS ²⁴	900	Exp.	3.0	15.0	35.0	33.0	15.0
		RRM	17.58	2.22	32.57	29.86	17.76
CPSE ²⁴	900	Exp.	2.0	10.0	32.0	38.0	18.0
		RRM	10.94	1.68	29.93	33.35	24.11

in the preceramic polymers and final pyrolysis temperature through redistribution reactions as indicated by eqs. (9)–(13).

CONCLUSIONS

When Blackglas™ ceramic is thermally treated in an inert atmosphere in the temperature range of 900–1350°C, the redistribution reactions involving Si—C and Si—O bonds change the microstructure of Blackglas™ ceramic. The RRM can be used to predict that

- As the pyrolysis temperature increases, the thermal redistribution reactions lead to the domains rich in SiO₄ and the domains rich in SiC₄ or a phase separation.
- The silicon oxycarbide phase may survive above 1400°C.
- The composition of silicon oxycarbide is very sensitive to the change of the O/Si ratio in the polymer precursors, and this can be used to modify material properties in a desirable way.

The RRM is in a good agreement with the experimental data and observation for both Blackglas™ and Nicalon.

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