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High-temperature behavior of silicon oxycarbide glasses in air environment

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Abstract

Silicon oxycarbide glasses (SiOC) have been produced by siloxane resin under flowing argon at 1000 °C and then their evolutions in air from 800 to 1700 °C were investigated. Those glasses annealed at various temperatures were characterized by X-ray diffraction, ^{29}Si MAS NMR, Raman spectroscopy, and chemical element analysis. It can be found that oxidation reactions of the SiOC glasses occurred at above 1000 °C; carbothermal reduction was indiscernible at temperature below 1600 °C but almost finished at 1700 °C; and the decomposition of SiO_xC_{4-x} network was complete at 1400 °C.

Keywords: Silicon oxycarbide; Glasses; Oxidation; High-temperature behavior

1. Introduction

Due to the wide range of possible applications, much attention has been paid to silicon oxycarbide glasses (SiOC) [1–3]. In their structure, divalent oxygen atoms are partially replaced by tetravalent carbon atoms and, thus enhance the mechanical and thermal properties of the material [4]. They are suitable materials for applications at high temperatures such as fibers or matrices for ceramic matrix composites [5,6]. SiOC glasses can be prepared by pyrolysis of polysiloxanes or sol–gel derived precursors. Its composition is usually reported as following equation: $SiC_xO_{2(1-x)} + yC_{free}$, where $SiC_xO_{2(1-x)}$ describes the amorphous silicon oxycarbide network and C_{free} is free carbon.

The need for environmentally stable applications motivated the development of silicon oxycarbide glasses [5]. Some applications (such as components for advanced space launch vehicles) concern high temperature utilization. However, these applications require exposure to oxidizing environment. Therefore there is a strong need to understand their high temperature behavior where decomposition or oxidation can take place in oxidizing environments. Sample size has been shown to affect the high temperature behavior of silicon oxycarbide glasses [7]. Indeed, many samples show different high temperature behavior such as aerogels, foams [8], fibers [9], coatings [10] and powders [11]. However, few studies have been devoted to the high temperature behavior of bulk SiOC glasses in oxidation environment.

In this article, we report the structure evolution of bulk SiOC glasses in air environment at temperature from 800 to 1700 °C, including oxidation behavior, bonds redistribution behavior, and carbothermal reductions.

2. Experimental procedure

Commercially available polymethyl(phenyl)siloxane resin (Dow Corning 249 flake resin) was cross-linked at 250 °C in air for 8 h, ball milled and finally sieved to particle size <75 μm. Green bodies were obtained by cold pressing of powder at 130 MPa. SiOC glasses were obtained through pyrolysis of green bodies in flowing high purity argon (purity ≥99.999%)with a heat rate of 20 °C/min up to 1000 °C held for 1 h. Then these glasses were in the furnace staring from room temperature and heating up to 800, 1000, 1200, 1400, 1600, and 1700 °C in laboratory air environment at a heating rate of 15 °C/min annealed for 1 h then cool down.

Quantitative elemental analysis (EA) of the samples was performed on LECO CS600 for C and TCH600 for O. The perchloric acid dehydration gravimetric method was adopted

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Table 1
Elemental analysis and char yield measured on samples after annealed at various temperatures.

Temperature (°C)	Yield (%)	Composition (wt%)			Oxycarbide stoichiometry
		O	C	Si	
a	–	27.14	35.10	36.81	SiO1.31C0.35 + C1.87
800	98.43	27.96	33.82	36.13	SiO1.35C0.32 + C1.84
1000	98.10	28.68	34.48	35.97	SiO1.39C0.30 + C1.86
1200	98.45	27.71	33.87	35.92	SiO1.35C0.32 + C1.83
1400	93.76	36.06	25.19	37.10	SiO1.70C0.15 + C1.54
1600	91.26	40.36	20.93	37.45	SiO1.88C0.06 + C1.24
1700	65.46	38.71	8.52	51.23	SiO1.32C0.34 + C0.05

a: Raw sample.

for the determination of Si content. X-ray diffraction (Bruker D8 advance) with Cu Kα radiation was used to verify the crystal phases. Raman spectra were obtained using a Confocal laser Microraman Spectrometer (Jobin Yvon LABRAM-HR) with a 514.5 nm line of laser. Microstructures induced by oxidation were analyzed by s (SEM; Hitachi S4800) and energy dispersive spectroscopy (EDS; EDAX Inc.) ^{29}Si MAS NMR spectra were measured with a Varian InfinityPlus 300 NMR spectrometer 59.56 MHz. The reference materials for chemical shift were tetramethysilane (TMS), and its chemical shift was adjusted to zero ppm. Spinning rates of the samples at a magic angle was 4.0 kHz, and recycle time was 30 s.

3. Results and discussion

The char yield and elemental analysis (EA.) results for SiOC glasses heat treated at various temperatures in laboratory air environment are reported in Table 1. It shows clearly that char yield and chemical composition values of SiOC are almost constant up to 1200 °C. From 1200 to 1600 °C, increasing ratio of O/Si and decreasing contents of C can be observed. This behavior is directly related to the oxidation of C_{free} and SiOC network. It is worth noting that once the temperature is above 1600 °C, an increasing ratio of C/Si can be observed. This behavior is resulting from carbothermal reductions occurring between SiO_2 and free carbon.

Raman spectra of SiOC samples before and after anneal at various temperature are reported in Fig. 1. Significant changes

Table 2
Raman characteristics of the free carbon in SiOC samples annealed at various temperatures.

Temperature	G peak		I_D/I_G
	position (cm^{-1})	half-width (cm^{-1})	
a	1607	58.9	1.59
800	1608	58.6	1.58
1000	1604	59.2	1.73
1200	1603	54.4	1.85
1400	1606	54.2	1.84
1600	1591	49.4	2.85
1625	1592	48.8	2.72
1650	1587	47.9	1.93
1675	1587	48.6	1.47

a: Raw sample.

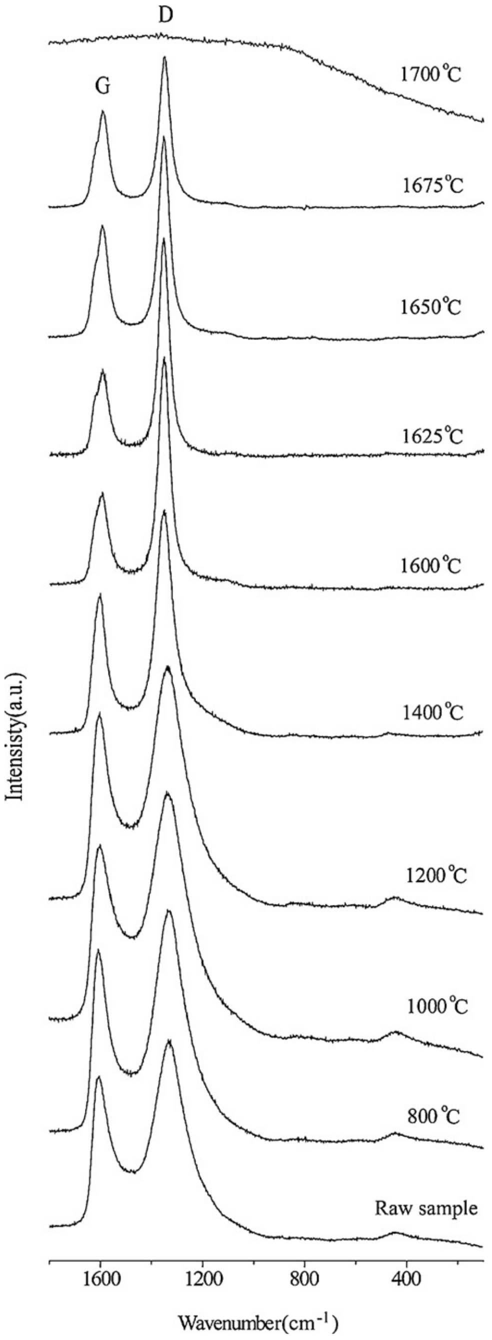

Fig. 1. Raman spectra of SiOC samples annealed in air environment at various temperatures.

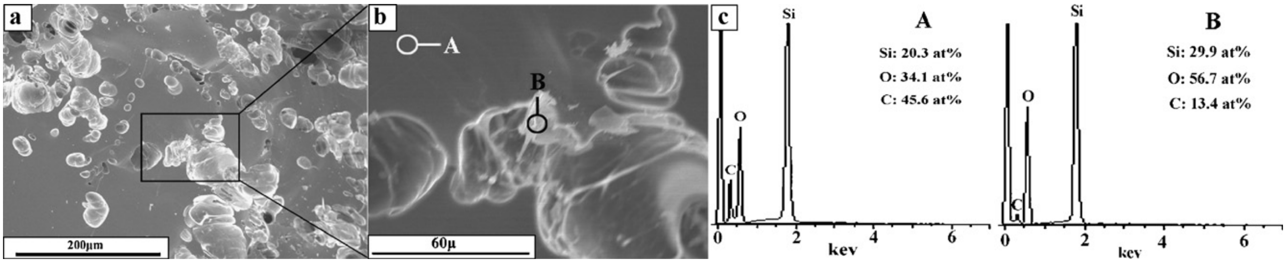

Fig. 2. 1000 °C oxidation. (a) Cross-section morphology. (b) Detail showing of oxidation region. (c) EDS spectra indicated in (b).

for spectral parameters such as peak position, half-width and the integrated intensity of different bands can be observed from 800 to 1700 °C. In order to determine those spectral parameters, band separation was performed employing Gauss–Lorentz function. The spectra were separated to the three bands at around 1335, 1535 and 1605 cm^{-1}. The bands centered at around 1605 and 1335 cm^{-1} are related to the G band and D band [12] and the band centered at around 1535 cm^{-1} reflects the presence of interstitial disorder site within the sample [13].

The peak position, half-width of G band and the ratio (I_D/I_G) are reported in Table 2. For those samples treated from 800 to 1675 °C, two trends can be found as follows: (i) the half-width reduce with increasing temperatures, it related to the increasing orientation of the carbon structure [14]. (ii) On increasing temperatures, the ratio (I_D/I_G) increased at first up to 1600 °C, and then decreased. The ratio (I_D/I_G) is related to the cluster diameter or in-plane crystallite size, La, of the free carbon domains, as reported by Tuinstra and Koenig ($I_D/I_G \propto La^{-1}$) for crystalline carbon [12] and recently by Ferrari and Robertson ($I_D/I_G \propto La^2$) for amorphous carbon [15,16]. Obviously, La will increase with the increasing temperatures. This suggests that, in those samples, the 1600 °C is the critical point of the microstructure evolution from amorphous carbon to graphite. It accord with the results reported by Ma recently [17]. For the sample treated at 1700 °C, no Raman signals can be detected. It indicates that the sample consist a smaller amount of, or without, free carbon.

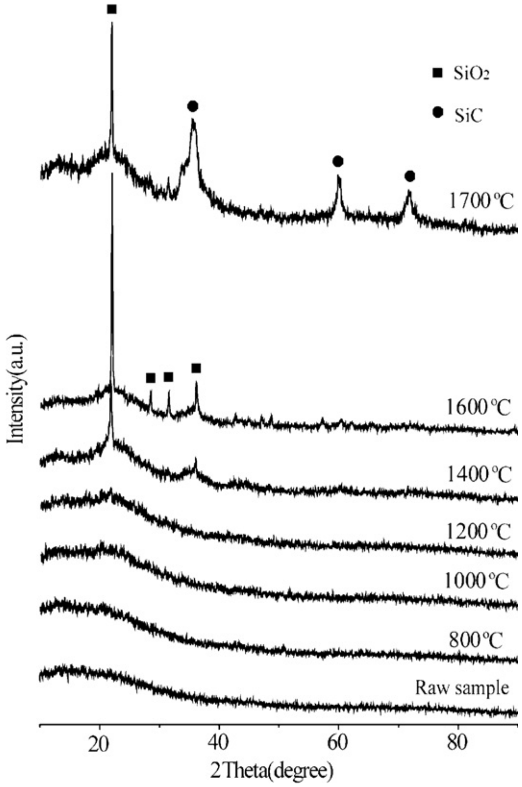

Fig. 3. XRD patterns of SiOC samples annealed in air environment at various temperatures.

After annealed at 1000 °C in a muffle furnace for 1 h, oxidation takes place in sample surface and the wall of open pores (Fig. 2 a). According to EDS analysis (Fig. 2c), the composition of the wall of open pores (B) is different from the composition of skeleton (A). Compare with the composition of A, B possess lower carbon contents and higher O/Si ratio. The lower contents of carbon indicated the oxidation of free carbon, and the higher ratio of O/Si showed the oxidation of SiOC network.

The X-ray diffraction patterns collected on samples before and after annealed at various temperatures are reported in Fig. 3. Both the raw sample and those samples treated at 800, 1000, and 1200 °C are typical of amorphous phases. At temperature above 1400 °C, cristobalite is present. It related to the oxidation of SiOC network. For the samples annealed at 1700 °C, β-SiC phase can be observed. It is due to carbothermal reductions occurring between SiO_2 and free carbon.

On increasing temperature, oxidation takes place in the surface of samples. At 1700 °C, the surface of samples was

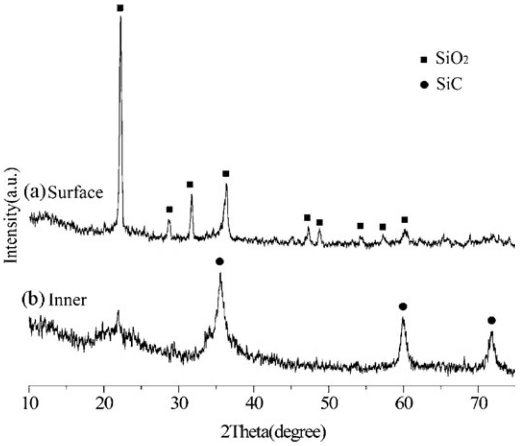

Fig. 4. XRD patterns of SiOC samples annealed at 1700 °C. (a) Collected on surface. (b) Collected on inner.

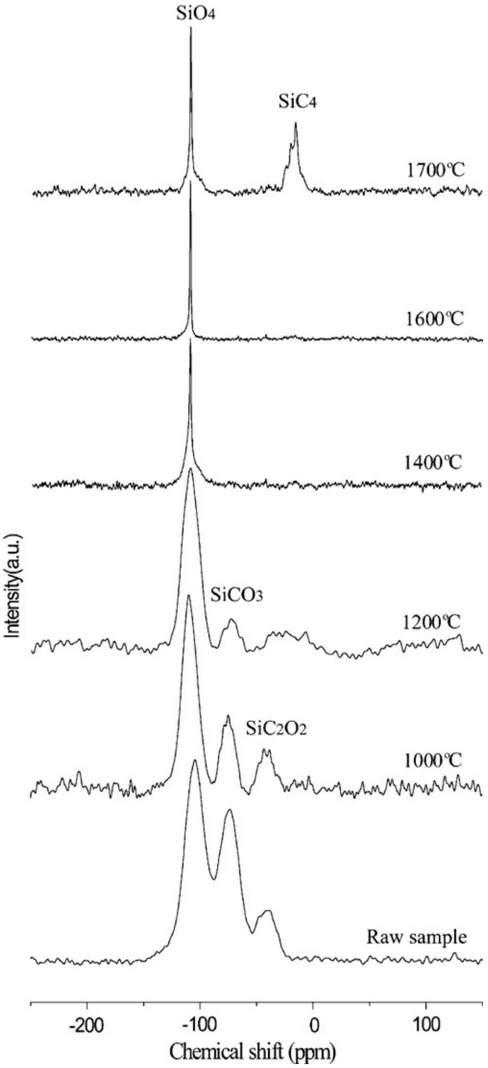

Fig. 5. ^{29}Si MAS NMR spectra of SiOC samples annealed in air environment at various temperatures.

covered by dense cristobalite, and thus the inner of sample was isolated from air. Indeed, spectra of the 1700 °C treated samples collected on the surface and inner, respectively, were reported in Fig. 4. It clearly show that the inner of samples mainly consist of SiC which is isolated from air by cristobalite on the surface.

The ^{29}Si MAS NMR spectra obtained from samples annealed at various temperatures are reported in Fig. 5. Depending on the annealing temperature, SiOC exhibits various amounts of the SiO_xC_{4-x} tetrahedral sites ($SiO_4 \sim -108$ ppm, $SiCO_3 \sim -74$ ppm, $SiC_2O_2 \sim -34$ ppm, $SiC_4 \sim -16$ ppm) [18]. The raw sample consists primarily of SiO_4, SiO_3C, and SiO_2C_2, with a smaller amount of, or without, $SiOC_3$ and SiC_4 units. On increasing the annealing temperature, the NMR data show a redistributing of bonds within the system. The evolution is gradual staring from 1000 °C to 1400 °C as seen by a decrease in $SiO_{4-x}C_x$ (where $1 \leq x \leq 2$) with respect to SiO_4 units. Additionally, at 1700 °C a peak emerges at around −16 ppm that is due to SiC_4 units. It is even possible to distinguish several peaks at −16, −20, and −25 ppm, which are due to the presence of crystalline β-SiC, with some α-SiC [19]. It indicated that the carbothermal reductions occurring between SiO_2 and free carbon is active in 1700 °C.

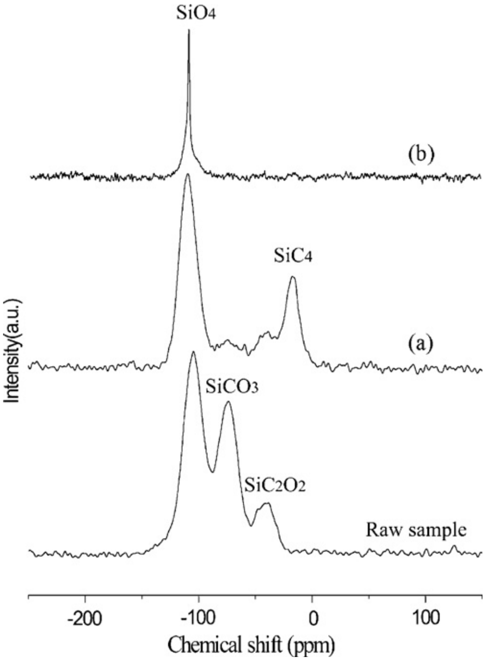

Fig. 6. ^{29}Si MAS NMR spectra of SiOC samples before and after annealed at 1400 °C. (a) Inert environment. (b) Air environment.

The presence of oxygen plays a crucial role on the bonds redistribution behavior of SiOC glasses. Spectra (Fig. 6) of the 1400 °C samples annealed in inert and air atmosphere, respectively, clearly shows the absence of SiC_4 units in air environment. For $SiC_xO_{2(1-x)}$ networks, at high temperatures reaction (1) [18] or reaction (2) [20] will be active leading to the formation of SiC in inert environment, and thus the SiC_4 units can be detected by NMR.

$$SiC_xO_{2(1-x)} \rightarrow SiO_2 + SiC \tag{1}$$

$$SiC_xO_{2(1-x)} \rightarrow SiC + SiO(g) + CO(g) \tag{2}$$

In air environment, as the generations of reaction (2) or (3), SiC will undergo an oxidation to generate SiO_2, leading to the absence of SiC_4 unite in NMR spectra. The overall reaction for the decomposition behavior is as depicted in reaction (3) [21]:

$$SiC_xO_{2(1-x)} + 3/2xO_2 \rightarrow SiO_2 + xCO(g) \tag{3}$$

Thus it is suggested that once the oxygen is present during the $SiC_xO_{2(1-x)}$ decomposition process, reaction (1) or reaction (2) will be replaced by reaction (3).

4. Conclusions

In this article, high-temperature behavior of silicon oxycarbide glasses in air was investigated. The following results were obtained: (i) on increasing the temperature Raman data show an increasing orientation of amorphous carbon in SiOC glasses, and free carbon was almost consumed at 1700 °C. (ii) Oxidations of free carbon and SiOC networks occur first at temperature above 1000 °C in sample surface and the wall of open pores. (iii) The presence of oxygen plays a crucial role on the decomposition behavior of SiO_xC_{4-x}. SiC_4 units are absent during the bonds redistribution process in air. (iv) β-SiC is formed in the inner of samples at 1700 °C. It is directly related to carbothermal reductions occurring between SiO_2 and free carbon.

Acknowledgements

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References

[1] S. Walter, G.D. Soraru, H. Brequel, S. Enzo, Microstructural and mechanical characterization of sol gel-derived Si-O-C galsses, J. Eur. Ceram. Soc. 22 (2002) 2389–2400.
[2] Y.D. Blum, D.B. MacQueen, H.-J. Kleebe, Synthesis and characterization of carbon-enriched silicon oxycarbides, J. Eur. Ceram. Soc. 25 (2005) 143–149.
[3] R. Zhuo, P. Colombo, C. Pantano, E.A. Vogler, Silicon oxycarbide glasses for blood-contact applications, Acta Biomater. 1 (2005) 583–589.
[4] C. Pantano, A. Singh, H. Zhang, Silicon oxycarbide glasses, J. Sol-Gel Sci. Technol. 14 (1999) 7–25.
[5] A.R. Bunsell, A. Piant, A review of the development of three generations of small diameter silicon carbide fibres, J. Mater. Sci. 41 (2006) 823–839.
[6] P.N. Adler, Overview of ARPA low-cost ceramic composites (LC3) program, in: 41st International SAMPE Symposium: Materials and process challenges—Aging systems, affordability, alternative applications, March 24–28, 1996, pp. 524–531.
[7] G.D. Soraru, D. Suttor, High temperature stability of sol-gel-derived SiOC galsses, J. Sol-Gel Sci. Technol. 14 (1999) 69–74.
[8] T. Takahashi, H. Munstedt, M. modesti, P. Colombo, Oxidation resistant ceramic foam from a silicone preceramic polymer/polyurethane blend, J. Eur. Ceram. Soc. 21 (2001) 2821–2828.
[9] M. Huger, S. Souchard, C. Gault, Oxidation of nicalon SiC fibres, J. Mater. Sci. Lett. 12 (1993) 414–416.
[10] M. Harris, T. Chaudhary, L. Drzal, R.M. Laine, Silicon oxycarbide coatings on graphite fibers: chemistry, processing, and oxidation resistance, Mater. Sci. Eng. A 195 (1995) 223–236.
[11] Y. Wang, H. Li, L. Zhang, L. Cheng, Oxidation behavior of polymer derived SiCO powders, Ceram. Int. 35 (2009) 1129–1132.
[12] F. Tuinstra, J.L. Koenig, Raman spectrum of graphite, J. Chem. Phys. 53 (1970) 1126–1130.
[13] T. Jawahari, A. Road, J. Casado, Raman spectroscopic characterization of some commercially available carbon black materials, Carbon 33 (1995) 1561–1565.
[14] S. Karlin, Ph. Colomban, Raman study of the chemical and thermal degradation of as-received and sol–gel embedded Nicalon and Hi-Nicalon SiC fibers used in ceramic matrix composites, J. Raman Spectrosc. 28 (1997) 219–228.
[15] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B 61 (20) (2000) 14095–14107.
[16] A.C. Ferrari, J. Robertson, Raman spectroscopy of amorphous, nanostructured, diamond-like carbon and nanodiamond, Philos. Trans. R. Soc. London, Ser. A 362 (2004) 2477–2512.
[17] Y. Ma, S. Wang, Z.-H. Chen, Raman spectroscopy studies of the high-temperature evolution of the free carbon phase in polycarbosilane derived SiC ceramics, Ceram. Int. 36 (2010) 2455–2459.
[18] H. Brequel, J. Parmentier, S. Walter, R. Badheka, G. Trimmel, S. Masse, J. Latournerie, P. Dempsey, C. Turquat, A. Desmartin-Chomel, L. Le Neindre-Prum, U.A. Jayasooriya, D. Hourlier, H.-J. Kleebe, G.D. Soraru, S. Enzo, F. Babonneau, Systematic structural characterization of the high-temperature behavior of nearly stoichiometric silicon oxycarbide glasses, Chem. Mater. 16 (2004) 2585–2598.
[19] F. Babonneau, G.D. Soraru, K.J. Thorne, J.D. Mackenzie, Chemical characterization of Si-Al-C-O precursor and its pyrolysis, J. Am. Ceram. Soc. 74 (1991) 1725–1728.
[20] T. Shimoo, K. Okamura, H. Takeuchi, Effect of reduced pressure on oxidation and thermal stability of polycarbosilane-derived SiC frbers, J. Mater. Sci. 38 (2003) 4973–4979.
[21] G. Chollon, Oxidation behaviour of ceramic fibres from the Si-C-N-O system and related sub-systems, J. Eur. Ceram. Soc. 20 (2000) 1959–1974.