Oxidation resistant ceramic foam from a silicone preceramic polymer/polyurethane blend

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Abstract

Silicon oxycarbide (SiOC) ceramic foams, produced by the pyrolysis of a foamed blend of a methylsilicone preceramic polymer and polyurethane (PU) in a 1/1 wt.% ratio, exhibit excellent physical and mechanical properties. The proposed process allows to easily modify the density and morphology of the foams, making them suitable for several engineering applications. However, it has been shown that, due to residual carbon present in the oxycarbide phase after pyrolysis, the foams are subjected to an oxidation process that reduces their strength after high temperature exposure to air (12 h 1200°C). A modified process, employing the same silicone resin preceramic polymer but a much lower PU content (silicone resin/PU = 5.25/1 wt.% ratio), has been developed and is reported in this paper. Microstructural investigations showed that carbon rich regions deriving from the decomposition of the polyurethane template are still present in the SiOC foam, but have a much smaller dimension than those found in foams with a higher PU content. Thermal gravimetric studies performed in air or oxygen showed that the low-PU containing ceramic foams display an excellent oxidation resistance, because the carbon-rich areas are embedded inside the struts or cell walls and are thus protected by the dense silicon oxycarbide matrix surrounding them. SiOC foams obtained with the novel process are capable to maintain their mechanical strength after oxidation treatments at 800 and 1200°C (12 h), while SiOC foams obtained with a higher amount of PU show about a 30% strength decrease after oxidation at 1200°C (12 h). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Foams; Oxidation; Polymer precursors; SiOC

1. Introduction

Processing technologies that utilize organic polymers to fabricate ceramics components have been proposed in the past in the literature.[1–3] The organic polymers have been mixed with the inorganic ceramic components, either ceramic powder or an inorganic monomer, as processing aids or sacrificial template matrices. The concept has already been applied to injection molding machines or for manufacturing uniquely shaped products. The key point is that the organic polymer helps the shaping process and then disappears during heating; the amount of organic component used depends on the role it has in the process (e.g. binder, volatile matrix, etc.). Ceramic foams have been produced using polyurethane (PU) and ceramic powder mixtures (so-called reticulated ceramics[4] or by a direct foaming process[5]), or acrylic monomers and ceramic powders (gel-casting[6]). Recently, Colombo and Modesti proposed a novel processing method for producing silicon oxycarbide (SiOC) ceramic foams, through the pyrolysis under an inert gas of foamed polymer blends of a preceramic polymer[7,8] (a silicone resin[9,10]) and an organic polymer (polyurethane).[11–14] The main concept behind this technology is the use of polyurethane, which is known to be easily foamed (physical or chemical blowing), as a structural template to produce the ceramic foam, in combination with a preceramic polymer. A process employing a different preceramic polymer has also been reported by Nangrejo et al.[15] The ceramic develops through the polymer-to-ceramic conversion of the silicone resins, which can be mixed in solution with the polyurethane

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precursors. The SiOC ceramic foams have a bulk density varying from 0.2 to 0.6 g/cc, a cell size in the 100–700 μm range, and exhibit very good mechanical properties.[11–14] Crushing strength, flexural strength and Young's modulus increase with increasing density of the material, and maximum values of about 16 MPa, 12 MPa and 7 GPa, respectively, have been so far obtained. The foams possess a coefficient of thermal expansion of 3.5×10^{-6} K^{-1} (20–1000°C) and display excellent thermal shock resistance properties. However, it has been shown that due to residual carbon present in the oxycarbide phase after pyrolysis, the foams are subjected to an oxidation process that reduces their strength after high temperature exposure to air for a comparatively long period of time (12 h 1200°C).[14] Our recent phase-morphological analysis of the foamed blend during the course of pyrolysis surprisingly indicated that the polyurethane did not constitute an interconnected continuos phase, but rather was dispersed as particles in a silicone resin-derived amorphous matrix.[16] In that study, silicone resin and polyurethane were used in a 1/1 wt.% ratio. In this paper we firstly investigated the possibility to obtain foamed blends using a silicone resin/PU weight ratio of 5.25/1. Secondly, we investigated the oxidation resistance of the low-PU-containing foams (5.25/1 weight ratio), and compared it to the material obtained with a higher PU content (1/1 weight ratio). The aim was to gain a deeper insight both into the foaming process and into the thermal stability of the SiOC ceramic foams obtained with this process, so that components with a specific morphology and oxidation resistance at high temperature could be developed for a range of engineering applications (e.g. filters, thermal shields, catalytic substrates, lightweight structural components).

2. Experimental

2.1. Materials

A foamed blend is a porous body consisting of a preceramic polymer and polyurethane. The preceramic polymer used here was a methylsilicone resin (SR350, General Electric Silicone Products Division, Waterford, NY). It is known that the methylsilicone resin can be converted to silicon oxycarbide (SiOC),[10] that is an amorphous ceramic material in which Si atoms are bonded to both O and C atoms, by pyrolysis between 1000 and 1400°C under inert atmosphere. Polyurethane precursors are polyether polyol and polymeric isocyanate. The polyol mixture was comprised of two polyether polyols (Tercacol 3 (hydroxyl number : 56 mg of KOH/g, viscosity at 25°C : 500 mPa·s, $M_w = 3000$ g/mol) and Tercarol 1 (hydroxyl number: 168 mg of KOH/g, viscosity at 25°C: 280 mPa·s, $M_w = 1000$ g/

mol), supplied by Enichem). The isocyanate was polyphenylmethane isocyanate (Tedimon 31, viscosity at 25°C: 180–250 mPa·s,%NCO: 31, supplied by Enichem). The reaction between the polyol mixture and the isocyanate gives rise to a semirigid PU, as reported in previous papers.[11–13] Amine catalysts, a solvent, and a surfactant were also used. The amine catalysts were bis(dimethylaminomethyl)ether and triethylenediamine in dipropylene glycol (Niax A-1 and A-33, supplied by OSi Specialties). The solvent was dichloromethane. The surfactant was polydimethylsiloxane (SC250 and SH205, supplied by OSi Specialties).

The foamed blend of SR350 and PU was prepared in two steps. The first step was the addition of SR350 dissolved in CH_2Cl_2 to the mixture of the polyols, the amine catalysts, the surfactant, and additional dichloromethane. The second step was the addition of polyisocyanate to the solution obtained in the first step. The expansion started during mechanical stirring by the evaporation of the solvent caused by the exothermal reactions occurring in the solution (physical blowing). In addition to that, water generated by the condensation reaction, promoted by the amine catalyst, of Si–OH groups in the silicone resin reacted with isocyanate, giving carbon dioxide gas that participated to the foaming (chemical blowing). Not only urethane bonds but also ureic bonds are formed through the reaction. It has to be mentioned that the silicone resin was pre-treated at 150°C before dissolving into dichloromethane, in order to reduce the amount of Si–OH groups present. After mechanical stirring, the foaming solution was poured in an open mold and kept in an oven at 30°C for several hours, for completing all the reactions. A more detailed preparation procedure has been already reported in previous papers.[11–13] The foams were prepared with a SR350/PU weight ratio of 1/1 or of 5.25/1. Foams with a silicone/PU weight ratio of 1/1 will be hereafter labeled High-PU foams, while foams with a 5.25/1 weight ratio will be labeled Low-PU foams. The foamed blends of SR350 and PU were pyrolyzed under nitrogen (99.999% N_2, 5.0 cc/min) for 1 h at 1200°C, with a heating rate of 2 K/min.

2.2. Pyrolysis and oxidation resistance investigations

The weight loss of unpyrolyzed foams (SR350/PU = 1/1, 5.25/1 weight ratio), cross-linked SR350, and PU foams was characterized by thermal gravimetric analysis (TGA) using a Netzsch STA409 thermobalance in air or nitrogen (99.999%) at a heating rate of 10 K/min. Some samples, pyrolyzed at 1200°C in N_2, were also isothermally hold for 12 h at 800 or 1200°C in air or oxygen. The foams were analyzed without milling them into powder. In the case of bulk SiOC glass (SR350 heated 1 h at 1200°C in N_2), the analysis was performed on powders with a diameter comprised

between 20 and 53 μm. The powder size was chosen in order to be similar to the cell wall thickness of the SiOC foams. TGA-FTIR (thermal gravimetric analysis connected with Fourier transform infrared spectroscopy) was used for the analysis of weight loss and decomposition gases of the pyrolyzed foams. The TGA measurements (thermal gravimetric analysis, TGA2950, TA Instruments) were conducted from room temperature to 1200°C, while the decomposition gases coming from the TGA cell were qualitatively analyzed with a FTIR spectrometer ((Magna-IR Spectrometer 750 with TGA interface, Nicolet) up to 1000°C. TGA analysis was performed using 70 ml/min of nitrogen (99.999% purity) flow and a heating rate of 10 K/min. The decomposition gases were transferred to the gas cell in the FTIR instrument through a transfer tube. Both the gas cell in the FTIR instrument and the transfer line were maintained at 200°C. The FTIR spectra were collected with a resolution of 4 cm^{-1} for 32 scans.

2.3. Phase morphology and microstructure analysis

The phase morphology of foamed blends of SR350/PU before and after pyrolysis was characterized by SEM (LEO435, LEO Elektronenmikroskopie GmbH, and Stereoscan 250 MK3, Cambridge Instruments). The linear dimensional variation of the foamed blend was measured using a Netzsch 402E dilatometer in flowing nitrogen at the heating rate of 10 K/min. The microstructure was characterized by X-ray diffraction (XRD) using a Philips 1730/1820 instrument (Cu K_α, 40 kV, 40 mA).

2.4. Mechanical characterization

The crushing strength of low- and high-PU foams of a selected bulk density, pyrolyzed at 1200°C and after being subjected to oxidation (12 h at 1200°C in air), was measured by compression testing, with a cross-head speed of 0.5 mm/min, on samples $6\times6\times12$ mm^3. The flexural strength was also determined, using a three-point bending fixture with a span of 30 mm and a cross-head speed of 0.5 mm/min. Both flexural and compression strength were measured at room temperature, using an Instron 1121 UTM. Each data point reported represents the average value of 10 individual tests.

3. Results and discussion

3.1. Foaming of SR350/PU blends and microstructure of foams

Previous papers[11–14,16] reported on the foaming of mixtures of SR350 silicone resin/PU, with a weight ratio of 1/1. After adjusting the Si-OH content by thermal

treatment, it was possible to obtain stable foams using also a SR350/PU solution with a 5.25/1 weight ratio. The foams maintained their morphology during pyrolysis, with no signs of melting or shape loss, indicating that the silicone resin was well crosslinked after blowing.[16] In Fig. 1 are reported SEM micrographs of an unpyrolyzed (a) and a pyrolyzed (b) low-PU foam. About 30% of cells in low-PU foams before pyrolysis display open-cell porosity, similarly to what was observed for high-PU foams,[11–13] and after pyrolysis most of the thin membranes closing the cell pores disappear. Average cell size for the pyrolyzed specimen of low-PU is about 50–70% larger than that for a high-PU. Possible explanations for this phenomenon include a different behavior of the surfactant agents in the low- and high-PU precursor mixture, the presence of less nucleation centers in the low-PU solution (nucleation occurs where the mixture becomes supersaturated with respect to the blowing agent, due to the polymerization reaction between polyol and isocyanate),[17] a lower viscosity of the low-PU solution (that would allow coalescence of the gas bubbles). Moreover, the lower linear
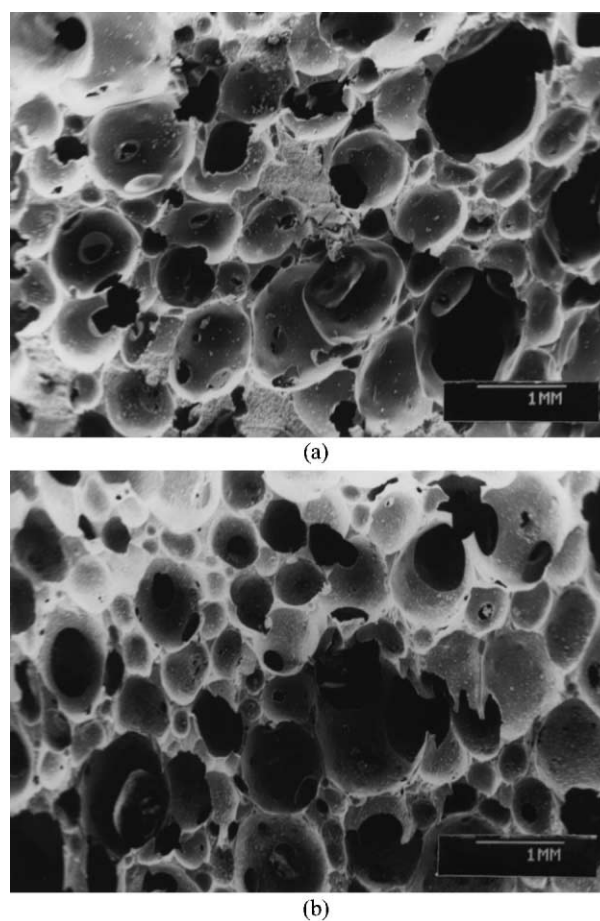

Fig. 1. (a) SEM micrograph of a low-PU unpyrolyzed foam (SR350/PU = 5.25/1 weight ratio). (b) SEM micrograph of a low-PU pyrolyzed foam (SR350/PU = 5.25/1 weight ratio).

shrinkage due to the lower PU amount in low-PU foams will result in larger cells after pyrolysis (see later).

As previously mentioned, our recent phase-morphological analysis on a foamed blend of SR350/PU with 1/1 weight ratio[16] showed that after foaming PU was dispersed as particles in the SR350 matrix. This was rather unexpected, and contrary to the original intention that PU would be used as a sacrificial template matrix. It was found, however, that the use of PU still enabled to control the morphology of the ceramic foam, in that by varying the PU precursors (polyols and isocyanate) one could obtain either flexible-, semi-rigid- or rigid-like structures.[11–13] The possibility of obtaining stable foams with a low PU content is another indication that its role in the process is not that of constituting a sacrificial template matrix. Indeed, SEM investigations showed that also in this case C-rich islands are found embedded within a Si-rich matrix.[16] Fig. 2(a) shows a topographical image of a high-PU foam before pyrolysis; the smooth wall surface of a cell (upper part), the slightly rough cross-section of a cell wall (middle part), and another cell (lower part) are visible. The roughness of the cross-section is caused by the preparation of the sample, broken by hand at room temperature. By analyzing using back-scattered electrons, the compositional image of the same place displayed in Fig. 2(a) was obtained, and is represented in Fig. 2(b). Dark islands, with a dimension of about 3–5 μm, are dispersed in a light matrix phase, not only in the wall surface but also in the cross-section of struts. Energy-dispersive X-ray analysis allowed to identify the light phase as Si-rich, hence deriving from the silicone resin, while the dark islands were mainly comprised of carbon, hence deriving from the PU.[16] The image shows that the SR350/PU blend is not miscible but has the sea/island morphology that is typical of a phase-separated structure.[18] Phase separation is mainly due to the difference of the surface tension of the two components (methyl silicone resin = 23 dyne/cm, polyurethane = 38 dyne/

cm).[19] Fig. 3(a) shows the topographical SEM image of the cross-section of a strut in a Low-PU foam before pyrolysis. The compositional image of the same area is reported in Fig. 3(b). Also in this case dark PU islands, with a dimension of about 1 μm, are dispersed in a light silicone-derived matrix phase.

It is important to observe that, in comparison to high-PU foams, the C-rich regions in the low-PU foams are much smaller. Also, in high-PU foams PU particles can be seen on the surface of cell walls, while no such particles are observed in that location in low-PU foams. This can be explained by the different PU content in the foams as well as by the surface tension difference between the SR350 silicone resin and PU.

We can hypothesize that the main role of PU in the foaming process is that of (i) homogeneously providing thermal energy to the liquid mixture for the physical evaporation of the solvent and (ii) controlling the viscosity of the solution (a condition necessary for obtaining a stable foam, influenced also by the initial rheological properties of the SR350 silicone resin).[16,20] An effect of the type of PU precursors on the morphology of the foam, as observed in high-PU foams,[11–13] will have to be demonstrated by further experiments in the case of low-PU foams.

3.2. Pyrolysis of foams

As reported in previous works,[11–14,16] during pyrolysis in inert atmosphere the polymer-to-ceramic transformation of the silicone resin occurs, yielding a silicon oxycarbide ceramic material, as well as the thermal decomposition of the PU component. The thermal gravimetric analysis curves reported in Fig. 4 indicate that the conversion process happens in two separate steps, around 300–400°C and 600–800°C. In the first step, decomposition of PU and volatilization of silicone oligomers occur, while in the second one the organic bonds in the silicone
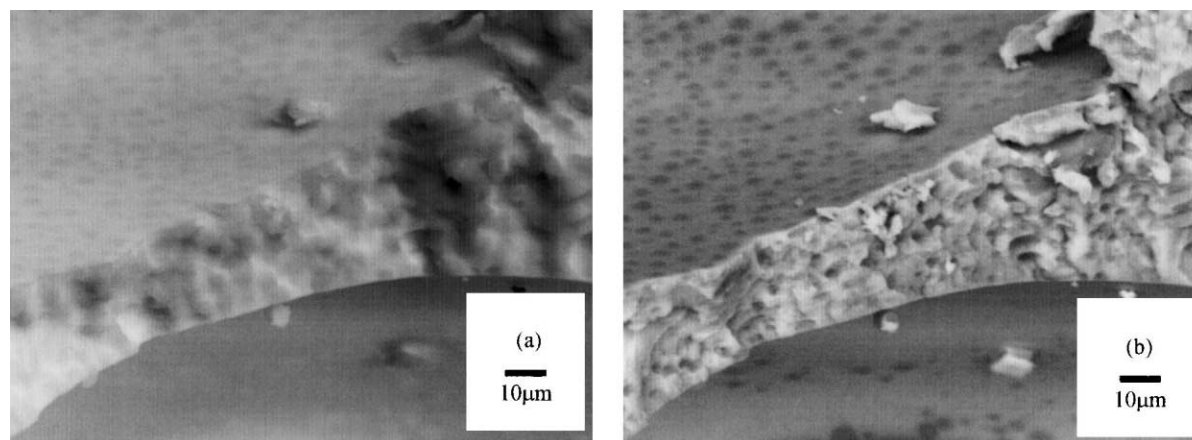

Fig. 2. (a) Topographical SEM image of an unpyrolyzed high-PU foam (SR350/PU = 1/1 weight ratio). The surface and the cross-section of a cell wall are shown. (b) Compositional SEM image (backscattered electrons) of an unpyrolyzed foam high-PU (SR350/PU = 1/1 weight ratio). The photo was taken at the same position as Fig. 2(a).
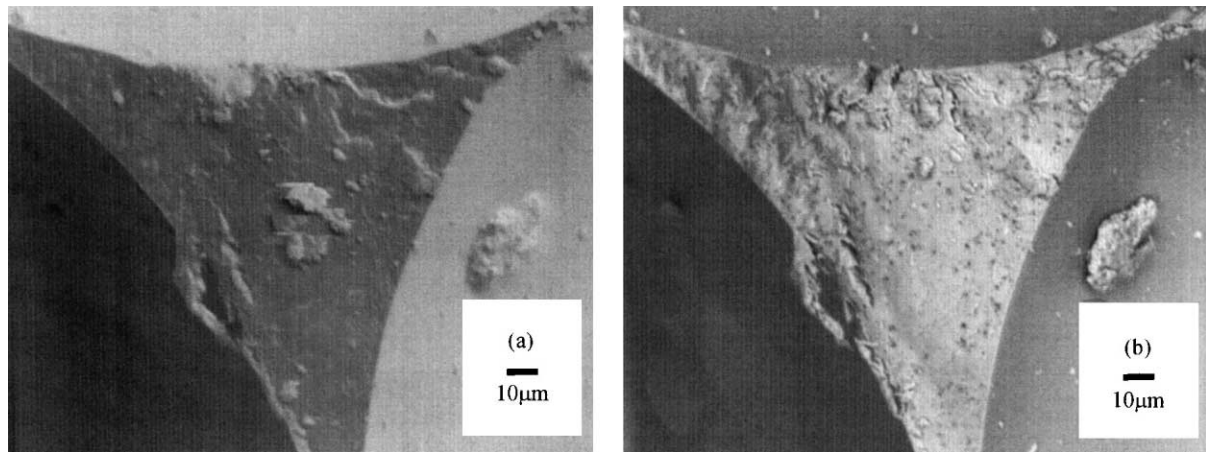
Fig. 3. (a) Topographical SEM image of an unpyrolyzed low-PU foam (SR350/PU = 5.25/1 weight ratio). The cross-section of a strut is shown. (b) Compositional SEM image of an unpyrolyzed low-PU foam (SR350/PU = 5.25/1 weight ratio). The photo was taken at the same position as Fig. 3(a).
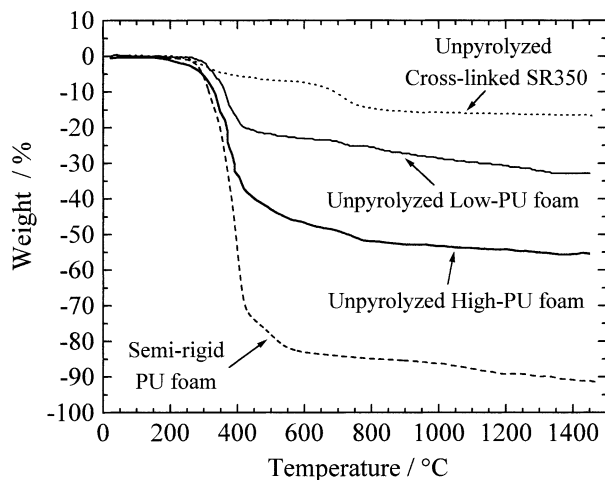

Fig. 4. TGA curves of unpyrolyzed SR350 (cross-linked), foamed semi-rigid PU, unpyrolyzed foamed blends of SR350/PU (low-PU: SR350/PU = 5.25/1 and high-PU: 1/1 weight ratio). Analysis performed under nitrogen.

resin are broken, with release of methane (ceramization).[16] The data show that PU decomposition leaves a carbonaceous residue (about 8 wt.%) within the SiOC material, while the ceramic yield of a pure SR350 material is about 84 wt.% at 1200°C. Calculated weight losses are in agreement with the experimental values (32 and 55 wt.% for the low- and high-PU foams, respectively) Calculated residual carbon from PU after pyrolysis in the low- and high-PU foams is, from TGA data, about 1.3 and 4 wt.%, respectively. Analysis of the total C content of pyrolyzed materials, performed with a LECO CS-244 carbon determinator, using an oxidation accelerator, gave 14.1±0.7, 16.2±0.6 and 29.6±0.9 wt.% for a bulk SiOC ceramic, a low-PU and a high-PU SiOC foams, respectively. Linear shrinkage upon pyrolysis, measured using a dilatometer, showed a contraction of about 35% (at 1200°C) for a high-PU foam,

while a low-PU foam at that temperature shrunk about 27%. The maximum dimensional changes occur in two steps (300–400 and 600–800°C range), in accordance with the TGA findings, the first interval is related to PU decomposition while the second one derives from the ceramization of the silicone resin.

3.3. Oxidation resistance

Low- and high-PU foams, pyrolyzed at 1200°C in N_2, were subjected to oxidation in the thermobalance, under air or oxygen. During heating from room temperature to 1200°C one can observe that the High-PU SiOC foam displays a sharp weight loss (about 2 wt.%) centered at about 600°C, while no significant variation is found for the low-PU foam (see Fig. 5). This effect is due to the oxidative reaction of the "free" carbon (i.e. the C atoms non directly bonded to the Si atoms but rather grouped together into turbostratic graphite clusters) embedded within the SiOC amorphous matrix,[8,10] as demonstrated by the FTIR analysis of the released gases, reported in Fig. 6. The peaks located at about 2300–2400 and 680 cm^{-1} are in fact attributable to CO_2. While part of these carbon clusters originate from the redistribution of bonds occurring in the silicone resin during the polymer-to-ceramic conversion,[8,10] it is evident that some are related to the carbonaceous residue of the PU component in the precursor mixture (see also Fig. 4).

The fact that virtually very limited weight loss is observed when the analysis was performed under nitrogen indicates that the thermal degradation of PU and the ceramization of SR350 silicone resin were virtually complete after pyrolysis for 1 h at 1200°C, and that no degradation mechanism (e.g. carbothermal reduction reactions) was active up to that temperature.

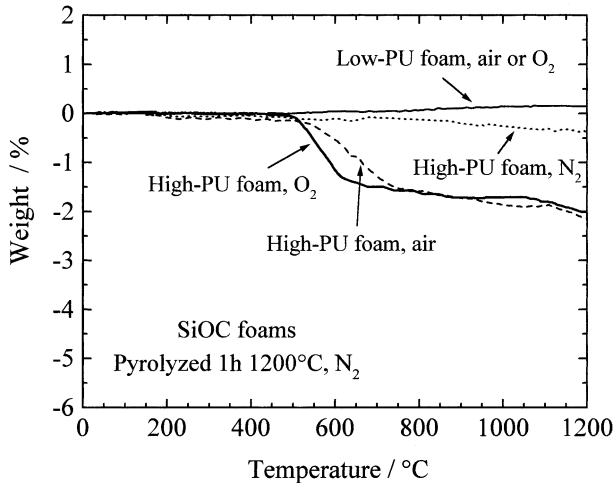A TGA investigation of the weight loss of low- and high-PU pyrolyzed foams as a function of time (up to 12

Fig. 5. TGA curves of SiOC foams which have been already pyrolyzed at 1200°C in N_2 (low-PU: SR350/PU = 5.25/1 and high-PU: 1/1 weight ratio). Analysis performed under nitrogen, air or oxygen.
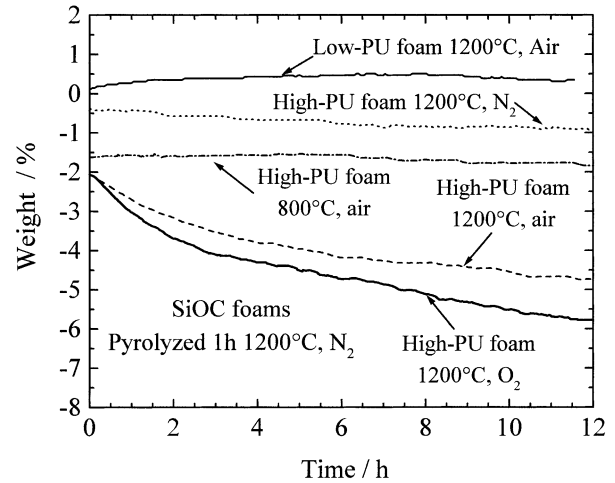

Fig. 7. Weight loss as a function of time for SiOC foams which have been already pyrolyzed at 1200°C in N_2 (low-PU: SR350/PU = 5.25/1 and high-PU: 1/1 weight ratio). Analysis performed under nitrogen, air, or oxygen.
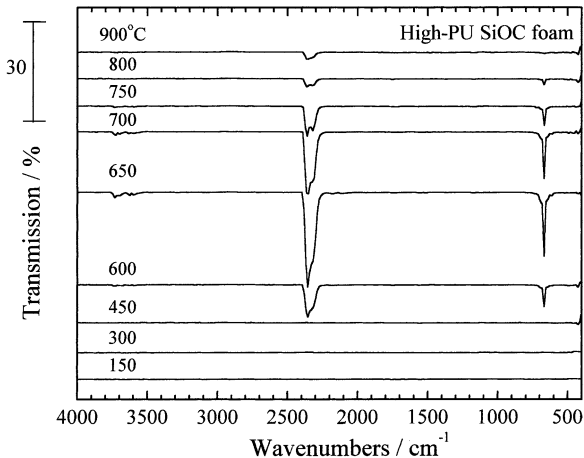

Fig. 6. FTIR spectra of released gases from a high-PU SiOC foam which have been already pyrolyzed at 1200°C in N_2 (SR350/PU = 1/1 weight ratio). Analysis performed under oxygen.

h, test performed at 800 and 1200°C) is reported in Fig. 7. Note that the curves do not start from weight loss zero because heating was performed under the testing atmosphere (air, oxygen) and thus the samples were already subjected to a weight loss before reaching the dwelling temperature (see Figs. 4 and 5). Again, the high-PU foam displayed a weight loss (about 3 and 4 wt.%) after 12 h at 1200°C under air and oxygen, respectively, while low-PU foam did not show any weight loss, but a very limited (0.4%) weight gain. While the weight loss is attributable to oxidation of the free C, the weight gain derives from the oxidation of Si–C bonds in the SiOC ceramic, to give SiO_2. In fact, in the experimental conditions adopted, both (free) carbon oxidation and Si–C bond oxidation are active.[21] Analysis of the total C content of oxidized materials (12 h at 1200°C, air), gave

14.9±0.7 and 24.7±0.6 wt.% for low-PU and high-PU SiOC foams, respectively.

It is interesting to observe that the data for oxidation of high-PU foam at 800°C indicate that, after the initial weight loss during heating, further oxidation of the material is hindered, possibly because oxygen diffusion is less favored at low temperatures (remember that no percolating carbon network is present in the material, see Fig. 2). Carbon analysis, in fact, gave a value of 29.2±0.5 for high-PU foam (12 h at 800°C, air). It has been demonstrated, however, that long term (i.e. 500 h) exposure at temperatures in the range 600–800°C are more damaging to SiOC ceramics because at those temperatures the (free) carbon oxidation predominates, while at higher temperatures the Si–C bond oxidation rate is comparable to that for carbon oxidation, leading to the formation of a silica-like protective surface layer.[21] Once more, the TGA data collected under N_2 showed that pyrolyzed SiOC foams are essentially thermally stable at high temperature under inert atmosphere.

The very high oxidation stability of low-PU foams is rather surprising since, from its C analysis and from the TGA data relative to high-PU foam, one would have expected about 1 wt.% weight loss. An explanation is possible when considering the results of the SEM investigations (see Figs. 1–3). A previous study of high-PU foams revealed that, during pyrolysis, the PU particles contained in the silicone-derived matrix gradually aggregated and tended to be disappear as the temperature increased, but carbon-rich regions remained present on the cell wall surface at all processing temperatures.[16] On the other hand, as mentioned before, low-PU foams showed no PU-derived traces on the cell wall surface, after pyrolysis at 1200°C. The higher oxidation stability of low-PU foams thus derives from the fact that these carbon-rich regions are fully embedded

within the silicon oxycarbide matrix. Indeed, TGA analysis performed on SiOC ceramic powder derived from the pyrolysis at 1200°C of pure SR350 silicone resin gave only a limited (about 0.7 wt.%) weight increase, after 12 h oxidation at 1200°C in air, indicating the very good oxidation resistance of the SiOC matrix material. A further confirmation of the hypothesis comes from TGA tests performed in air or oxygen on a powder obtained from a low-PU foam. In this case, a 0.3 wt.% weight loss, located at about 600°C, was observed, showing that crushing the low-PU foam exposed the carbon-rich areas within the struts to the testing atmosphere. Another reason for the different oxidation behavior of low- and high-PU pyrolyzed foams is that the oxidation of the more numerous carbon-rich islands, possessing also a higher domain size, in the case of high-PU foams leads to a higher porosity throughout the SiOC material with an increase of the surface area. Besides the overall free carbon content, a possible influence of the different morphology of the two types of foams (strut size, cell wall thickness, dimension of the holes in the cell walls), yielding varying diffusion path lengths for oxygen, should also be considered.

In agreement with the above findings and discussion, XRD analysis, performed on specimens before and after oxidation, show that cristobalite crystals formed in high-PU SiOC foams oxidized at 1200°C, while no microstructural change occurred in low-PU foams or, in high-PU foams, after oxidation at 800°C (see Fig. 8). The same oxidation treatments performed on a pure
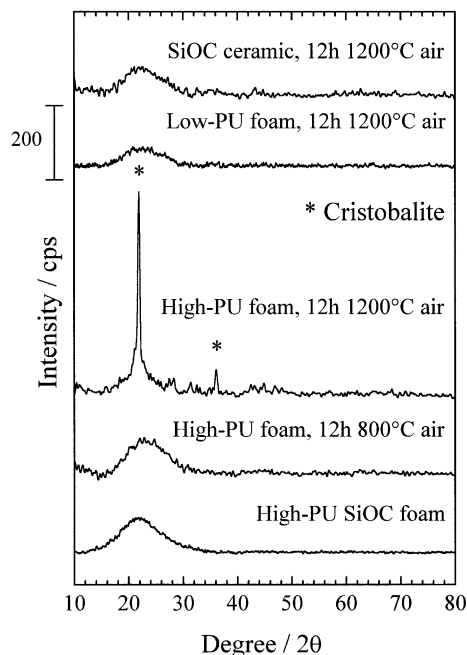
Table 1
Mechanical properties (MPa) of low- and high-PU SiOC foams, of similar bulk density, as pyrolyzed or after an oxidation treatment (12 h 800 or 1200°C, air)

	High-PU SiOC foam	Low-PU SiOC foam
Flexural strength, as pyrolyzed	3.69±0.28	2.70±0.40
Crushing strength, as pyrolyzed	3.32±0.74	2.02±0.84
Flexural strength, oxidized 12 h 800°C	3.73±0.97	2.50±0.80
Crushing strength, oxidized 12 h 800°C	2.98±0.67	1.80±0.50
Flexural strength, oxidized 12 h 1200°C	2.29±0.31	3.00±0.50
Crushing strength, oxidized 12 h 1200°C	2.33±0.75	2.04±0.75

(powdered) SiOC ceramic, obtained from the direct pyrolysis at 1200°C in N_2 of SR350 silicone resin, did not affect its microstructure, and the specimen remained amorphous. Evidently, the burn-off of carbon from the high-PU foams' structure led to the formation of active nucleation sites for silica. The different PU content did not affect the microstructure of as-pyrolyzed specimens, which are both amorphous, and no carbon phases are detectable in the diffraction patterns, probably because of its the limited amount. The patterns for low-PU foams pyrolyzed and oxidized 12 h at 800°C were not reported in Fig. 8 because they are identical to the displayed data for the low-PU specimen oxidized 12 h at 1200°C.

The influence of different oxidation resistance between low- and high-PU foams on the mechanical properties is shown in Table 1. SiOC ceramic foam bars of similar bulk density (0.4±0.02 g/cc) were tested before and after oxidation at various temperatures. A decrease in strength in high-PU foams after oxidation at 1200°C is evident (about 30%), and it is linked to both crystallization and porosity formation within the struts of the material,[14] while the strength of low-PU foams remained unaffected by the treatment, in accordance with the TGA and XRD results. Correspondingly, no strength decrease in high-PU foams was observed after oxidation at 800°C. The strength difference between low- and high-PU SiOC foams of similar density can depend on the different cell size of the two materials[22] (about 730±205 μm for the low-PU foam versus about 430±116 μm for the high-PU foam), but a larger set of specimens of various densities will have to be tested to clarify this issue.

Fig. 8. XRD patterns for SiOC foams (low-PU: SR350/PU = 5.25/1 and high-PU: 1/1 weight ratio) and SiOC ceramic powder, pyrolyzed at 1200°C in N_2, as received or after oxidation for 12 h at 800 and 1200°C in air.

4. Conclusions

In this paper we demonstrated the possibility to obtain silicon oxycarbide ceramic foams starting from a mixture containing a much lower polyurethane content than reported before. The polyurethane helps the blowing process by homogeneously providing thermal energy to the liquid mixture for the physical evaporation of the

solvent, and by controlling the viscosity of the solution. The advantage of this process modification lies in the fact that produced SiOC foams have a lower overall free carbon content, and thus display a much higher oxidation stability at high temperature. Carbon-rich areas have a limited size and are fully embedded within the dense silicon oxycarbide matrix. In the case of SiOC foams obtained from a solution with a low PU content, mechanical properties are retained after oxidation at 1200°C, while a strength decrease is observed for SiOC foams obtained from a solution with a high PU content.

Acknowledgements

References

1. Grader, G. S. and Zuri, L., Tape casting slip preparation by in situ polymerization. *J. Am. Ceram. Soc.*, 1993, **76**, 1809–1814.
2. Nakanishi, K. and Soga, N., Phase separation in gelling silica-organic polymer solution: systems containing poly(sodium styrenesulfonate). *J. Am. Ceram. Soc.*, 1991, **74**, 2518–2530.
3. Saito, K., Arakida, Y. and Inoue, M., *Injection Molding Technology of Fine Ceramics*. Nittkan Kogyou Shinbun, Tokyo, 1987 p. 213..
4. Saggio-Woyansky, J., Scott, C. E. and Minnear, W. P., Processing of porous ceramics. *Am. Ceram. Soc. Bull.*, 1992, **71**, 1674–1682.
5. Peng, H. X., Fan, Z., Evans, J. R. G. and Busfield, J. J. C., Microstructure of ceramic foams. *J. Eur. Ceram. Soc.*, 2000, **20**, 807–813.
6. Sepulveda, P. and Binner, J. G. P., Processing of cellular ceramics by foaming and in situ polymerization of organic monomers. *J. Eur. Ceram. Soc.*, 1999, **19**, 2059–2066.
7. Baney, R. and Chandra, G., *Encyclopedia of Polymer Science and Engineering, Preceramic Polymers*. John Wiley & Sons, New York, 1988 pp. 312-344..
8. Riedel, R., *Materials Science and Technology, Advanced Ceramic from Inorganic Polymers*. VCH, Weinheim, 1995 pp. 1–50.
9. Baney, R. H., Itoh, M., Sakakibara, A. and Suzuki, T., Silsesquioxanes. *Chem. Rev.*, 1995, **95**, 1409–1430.
10. Renlund, G. R., Prochazka, S. and Doremus, R. H., Silicon oxycarbide glasses: part I. Preparation and chemistry. *J. Mater. Res.*, 1991, **6**, 2716–2722 and Renlund, G. R., Prochazka, S. and Doremus, Silicon oxycarbide glasses: part II. Structure and properties. *J. Mater. Res.*, 1991, **6**, 2723–2734.
11. Colombo, P., Griffoni, M. and Modesti, M., Ceramic foams from a preceramic polymer and polyurethanes: preparation and morphological investigations. *J. Sol-Gel Sci. Technol.*, 1998, **13**, 195–199.
12. Colombo, P. and Modesti, M., Silicon oxycarbide ceramic foam from a preceramic polymer. *J. Am. Ceram. Soc.*, 1999, **82**, 573–578.
13. Colombo, P. and Modesti, M., Silicon oxycarbide foams from a silicone preceramic polymer and polyurethane. *J. Sol-Gel Sci. Technol.*, 1999, **14**, 103–111.
14. Colombo, P., Shelleman, D.L. and Hellmann, J.R., Mechanical properties of silicon oxycarbide ceramic foams, submitted to *J. Am. Ceram. Soc.*
15. Nangrejo, M. R., Bao, X. and Edirisinghe, M. J., Preparation of silicon carbide-silicon nitride composite foams from pre-ceramic polymers. *J. Eur. Ceram. Soc.*, 2000, **20**, 1777–1785.
16. Takahashi, T., Münstedt, H., Colombo, P. and Modesti, M., Thermal evolution of a silicon resin/polyurethane blend from preceramic to ceramic foam. *J. Mater. Sci.*, in press.
17. Niyogi, D, Kumar, R. and Gandhi, K. S., Modeling of bubble-size distribution in free rise polyurethane foams. *AIChE J.*, 1992, **38**, 1170–1184.
18. Utracki, L. A., *Polymer Alloys and Blends, Thermodynamics and Rheology*. Carl Hanser Verlag, Munuch, 1989 p. 131.
19. Brandrup, J. and Immergut, E. H., *Polymer Handbook,* 3rd edn. John Wiley & Sons, New York, 1989, p. VI/422.
20. Takahashi, T., Kaschta, J. and Münstedt, H., Melt rheology of silicone preceramic polymer and its structure. Submitted to *Rheol. Acta.*
21. Brewer, C. M., Bujalski, D. R., Parent, V. E., Su, K. and Zank, G. A., Insights into the oxidation chemistry of sioc ceramics derived from silsequioxanes. *J. Sol-Gel Sci. Technol.*, 1999, **14**, 49–68.
22. Morgan, J. S., Wood, J. L. and Bradt, R. C., Cell size effect on the strength of foamed glass. *Mater. Sci. Eng.*, 1981, **47**, 37–42.