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Processing and characterization of particles reinforced Si–O–C composites via pyrolysis of polysiloxane with SiC or/and Al fillers

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Abstract

Polysiloxane loaded with SiC as inert filler, and Al as active filler, was pyrolyzed in nitrogen to fabricate Si–O–C composites, and the processing and properties of the filled Si–O–C composites were investigated. Adding SiC fillers could reduce the linear shrinkage of filler-free cured polysiloxane in order to obtain monolithic SiC/Si–O–C composites. The flexural strength of SiC/Si–O–C composites reached 201.3 MPa at a SiC filler content of 27.6 vol.%. However, SiC/Si–O–C composites exhibited poor oxidation resistance, thermal shock resistance and high temperature resistance. Al fillers could react with hydrocarbon generated during polysiloxane pyrolysis at 600 °C and N_2 at 800 °C to form Al_4C_3 and AlN, respectively. The volume expansions resulting from these two reactions were in favor of the reduction in linear shrinkage and the improvement in flexural strength of SiC/Si–O–C composites. The flexural strength of Al-containing SiC/Si–O–C composites was 1.36 times that of SiC/Si–O–C composites without Al at an Al filler content of 20 vol.%. The addition of Al fillers remarkably improved the high temperature resistance and oxidation resistance of SiC/Si–O–C composites, but not thermal shock resistance.

Keywords: A. Precursors; C. Mechanical properties; C. Thermal shock resistance; Silicon oxycarbide; Oxidation; Thermal stability; Filler; Ceramic-matrix composites

1. Introduction

Manufacturing of ceramic materials via pyrolysis of preceramic polymers has been investigated for more than 20 years. The preceramic polymer route offers numerous advantages over conventional processing methods. These include processing versatility (e.g., plastic forming ability), lower processing temperature, high purity, and preparation of metastable phases unachievable by conventional methods. Furthermore, although techniques for preceramic polymer synthesis can be complex, polymer compositions and structures can be tailored to yield the desired ceramic upon pyrolysis through careful control of synthesis parameters.

Many different Si-based preceramic polymers have been discovered since their original development by Yajima et al. [1]. Of these precursors, polysiloxane (PSO) has attracted increasing interest in recent years. It is not only commercially available but also very cheap, and its derived silicon oxycarbide (Si–O–C) (in Ar or N_2) and silicon oxynitride (Si–N–O) (in NH_3) ceramics have been demonstrated to possess improved properties such as creep resistance and microstructural stability over those of many conventional silicate ceramics [2,3]. Therefore, PSO is considered as a desirable precursor for low-cost ceramic materials with high performance.

The usefulness of preceramic polymers as precursors to surface coatings or fibers has been well recognized, however, the application of preceramic polymers to fabricate dense ceramic matrices and monolithic bodies is still limited. Basic limitations for bulk component fabrication from preceramic polymers result from the extraordinary high volume shrinkage and a pronounced density increase following the polymer–ceramic conversion. For example, density typically increases by a factor of 2–3 from the precursor (1 g/cm^3) to the ceramic residue (SiO_2, 2.2–2.6 g/cm^3;

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Si_3N_4 and SiC, 3.0–3.2 g/cm^3), and volume shrinkage exceeds 50%, which usually result in extended cracking and pore formation in the pyrolyzed products and destroy the integrity of the component. Thus, direct conversion of a polymer compact to a dense ceramic compact is almost impossible to achieve.

In order to reduce the shrinkage and porosity upon pyrolysis, suitable fillers can be incorporated into preceramic polymers. Two types of fillers may be chosen, one that remains inert during pyrolysis, and the other that reacts with the pyrolysis gases and/or atmosphere to form nitrides and/or carbides. The former is called inert filler that reduces shrinkage according to the filler volume effect and the latter is referred to as active filler that can compensate shrinkage by appropriate filler expansion. SiC, B_4C, Si_3N_4, or BN are the most often used inert fillers [4]. Greil [5] have studied several active fillers and their effects on reducing the shrinkage of preceramic polymers.

In the present work, SiC as inert filler, and Al as active filler, were incorporated into polysiloxane that was used as a precursor to Si–O–C ceramics. The processing and properties of the filled Si–O–C composites were investigated.

2. Experimental procedure

PSO, a colorless transparent liquid containing 1.4 wt.% hydrogen, was selected as the precursor to Si–O–C ceramics. Divinylbenzene (DVB), a light yellow transparent liquid, was selected as the cross-linking reagent for PSO. Chloroplatinic acid (H_2PtCl_6), dissolved in anhydrous ethanol, was used as the catalyst. The viscosities of PSO and DVB at room temperature were 24 mPa·s and less than 10 mPa·s, respectively. The cure and pyrolysis behaviors of PSO/DVB were reported earlier [6–8].

PSO and DVB were mixed and stirred vigorously. During stirring, H_2PtCl_6/ethanol solution was dropped into PSO/DVB solution. After stirring for a period of time, β-SiC powders with a mean particles size of 0.4 μm and Al powders with a mean particles size of 5 μm were dispersed into PSO/DVB solution by vigorous stirring. Specimens of rectangular shape were formed by pressureless casting of the polymer-filler mixtures into modular molds of steel, followed by thermal-induced curing of the polymer matrix at 120 °C for 6 h. The green compacts were pyrolyzed under flowing high purity nitrogen (99.999%). A heating cycle involved heating up to 300 °C at 2 °C/min, holding at this temperature for 1 h, a second ramp at 0.5 °C/min up to 1100 °C with a 1 h hold and final cooling at 1 °C/min. After the first pyrolysis, three cycles of vacuum infiltration-curing-pyrolysis of PSO/DVB solution were conducted to densify the composites.

The bulk densities of the resultant composites were measured according to Archimedes' principle with deionized water as immersion medium. Each data point was an average over eight values. Linear shrinkage was defined as the ratio of the difference between the size of the resultant composites and that of the green compact to the size of the green compact. Phase composition was determined by X-ray diffraction using Cu Kα radiation with a nickel filter. Pyrolysis behavior of cured Al-filled PSO/DVB up to 1600 °C in nitrogen was investigated by thermal gravimetric analysis (TGA) carried out with a NETZSCH STA 449C Thermal System at 10 °C/min. A high purity nitrogen flow (20 cm^3/min) was used prior to and during pyrolysis. Flexural strengths were measured by a three-point bending method from rectangular bars (3 mm × 4 mm × 35 mm) with the span/height ratio of 10 and a cross-head speed of 0.2 mm/min. For flexural strength tests, five bars were measured for each composite. After the flexure tests, scanning electron microscopy (SEM) was employed to observe the fracture surfaces of the composites.

3. Results and discussion

3.1. Properties of SiC/Si–O–C composites derived from SiC-filled polysiloxane

Table 1 shows the densities, linear shrinkage and flexural strengths of SiC/Si–O–C composites with various content of SiC powders. It can be seen that the filler-free PSO/DVB suffered a total linear shrinkage of 25.0% during pyrolysis, which resulted in extended cracking and pores in the pyrolysates and destroyed the integrity of the pyrolysates. Therefore, direct conversion of PSO/DVB to a dense Si–O–C ceramics is almost impossible to achieve. It was found that a SiC powder content higher than 11.8 vol.% (30 wt.%) was necessary to produce sound monolithic SiC/Si–O–C bodies. When the content of SiC powders was more than 31.9 vol.% (60 wt.%), the suspension showed a high viscosity, leading to inhomogeneous distribution of SiC powers in suspension

Table 1
Densities and properties of SiC/Si–O–C composites with various content of SiC powders

Sample	Content of SiC powders (vol.%)	Density (g/cm^3)	Theoretical density (g/cm^3)	Linear shrinkage (%)	Flexural strength at room temperature (MPa)
S0	0	1.900	–	25.0	–
S40	17.2	2.103	2.345	13.0	142.9
S50	23.8	2.167	2.470	11.2	200.3
S55	27.6	2.194	2.535	9.4	201.3

Remark: Content of SiC powders was referred to as the volume ratio of SiC powders to (PSO + DVB + SiC).

and distortion and cracking during pyrolysis. So, 17.2 vol.% (40 wt.%), 23.8 vol.% (50 wt.%), and 27.6 vol.% (55 wt.%) of SiC powders were dispersed into PSO/DVB solution to fabricate SiC/Si–O–C composites, and the corresponding composites were denoted as sample S40, S50, and S55, respectively.

As shown in Table 1, incorporating SiC fillers reduces the linear shrinkage of filler-free PSO/DVB remarkably. With the increase of the content of SiC fillers, the linear shrinkage was reduced gradually. At the same time, the flexural strength of SiC/Si–O–C composites increased with increasing the content of SiC fillers. The filler-loaded PSO/DVB exhibited a pronounced reduction of linear shrinkage to 9.4% and the flexural strength of SiC/Si–O–C composites reached 201.3 MPa at a SiC filler content of 27.6 vol.%. However, it can be noted from Table 1 that the densities of sample S40, S50, and S55 were only 89.7%, 87.7%, and 86.5% of their theoretical densities, respectively. Similar to most porous ceramic materials, flexural strength data can be fitted by the Ryske-witch expression [5],

$$\sigma = 630\exp(-5Vp)$$

suggesting a further potential for increasing flexural strength with decreasing porosity. The residual pores mainly resulted from the inclusion of air during pressureless casting and the nondispersed fillers agglomerates. Improved processing could result in enhanced mechanical properties of SiC/Si–O–C composites, which will be investigated in subsequent studies.

The oxidation resistance, thermal shock resistance and high temperature resistance of SiC/Si–O–C composites were characterized by the comparison between the flexural strengths before and after oxidation at 1100 °C for 10 h under static air, five times of thermal shock from 1100 °C to room temperature under static air and heat treatment at 1500 °C for 2 h under flowing nitrogen. The results are presented in Table 2.

As shown, SiC/Si–O–C composites exhibited poor oxidation, thermal shock and high temperature resistances. In SiC/Si–O–C composites fabricated at 1100 °C, Si–O–C matrix consisted of [SiO_xC_{4-x}] ($0 \leq x \leq 4$) metaphase and free carbon whose content was 26.3 wt.% [6–8]. When SiC/Si–O–C composites were exposed under static air at 1100 °C for 10 h, the free carbon was completely oxidized by O_2 that diffused easily into composites through pores, decreasing the densities and hence impairing the flexural strength of SiC/Si–O–C composites. After thermal shock treatment, SiC/Si–O–C composites exhibited lower remaining flexural strength than that after oxidation, which could be ascribed to the oxidation of free carbon under air and the mismatch of thermal expansion coefficients between SiC fillers ($4.5 \times 10^{-6}\,K^{-1}$) and Si–O–C matrix ($1.2 \times 10^{-6}\,K^{-1}$) [9]. In previous studies [6–10], it had been reported that Si–O–C matrix could be stable to 1200 °C and transformed to [SiO_4] and [SiC_4] at 1400 °C as a result of redistribution reaction and a carbothermal reduction into SiO_2, SiC, SiO, and CO. Thus, many pores were created in SiC/Si–O–C composites due to the evolution of SiO and CO when heated at 1500 °C for 2 h under nitrogen atmosphere. As shown in Fig. 1, large quantities of interconnected micropores were observed in composites after heat treatment, which accounted for the decrease in flexural strength.

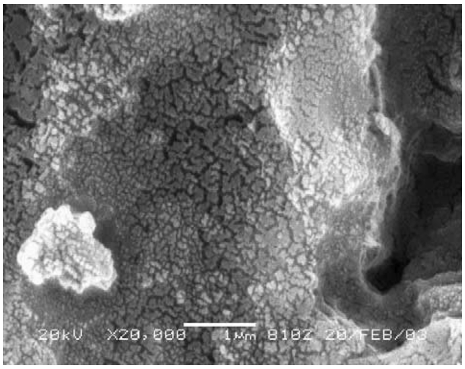

Fig. 1. SEM photo of fracture surface of SiC/Si–O–C composites after heated under nitrogen at 1500 °C for 2 h.

3.2. Pyrolysis of Al-filled PSO/DVB

Reactivity of the Al and PSO/DVB under nitrogen was studied using thermogravimetry and XRD. The results are shown in Figs. 2 and 3. As shown in Fig. 2(a), a gradual weight gain occurred at above 800 °C when Al powders were heated in nitrogen, indicating that nitrogen can be employed to nitride the Al powders at a temperature above 800 °C. In Fig. 2(b), the gradual weight gain at above 800 °C was also observed when the Al-filled PSO/DVB was pyrolyzed in nitrogen. It can be noted that there was little weight loss (0.3%) between 600 and 800 °C, which was different from the weight loss (5.5%) of filler-free PSO/DVB [6,7]. The XRD results (Fig. 3) showed that the Al fillers transformed to Al_4C_3 at 600 °C. The formation of Al_4C_3 was due to the reaction between Al and the hydrocarbon or

Table 2
Oxidation, thermal shock and high temperature resistances of SiC/Si–O–C composites

Content of SiC fillers (vol.%)	Flexural strength (MPa)					
	Oxidation resistance		Thermal shock resistance		High-temperature resistance	
	Before	After	Before	After	Before	After
17.2	142.9	60.7	142.9	–	142.9	24.1
27.6	201.3	62.0	201.3	38.7	201.3	16.0

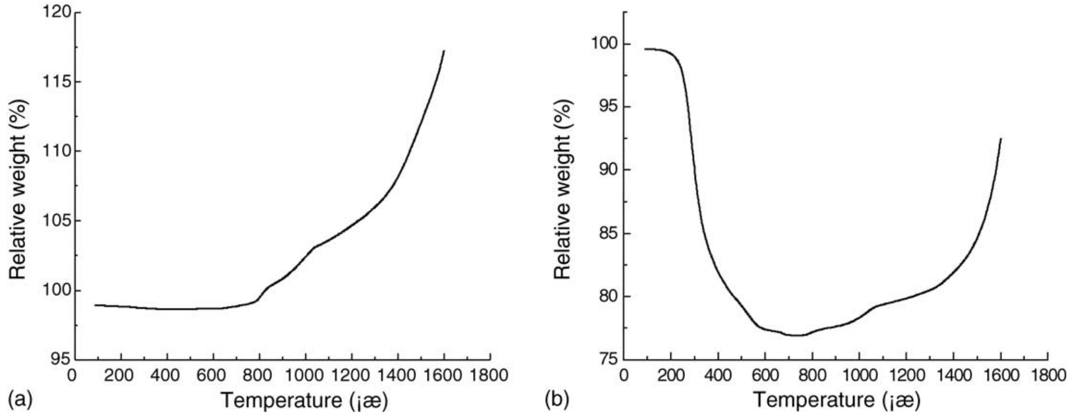

Fig. 2. Thermogravimetric analysis of Al powders (a) and Al-filled PSO/DVB (b) when heated from room temperature to 1600 °C under flowing nitrogen.

carbon pyrolysis products of PSO/DVB since the nitridation of Al began at 800 °C. From the point of view of thermodynamics, the reactions between Al and the hydrocarbon or carbon pyrolysis products can occur at 600 °C. If the Al is carburized through a gas-phase reaction with CH_4, the following reaction is expected:

$$4Al(s) + 3CH_4(g) \rightarrow Al_4C_3(s) + 6H_2(g)\uparrow \quad (1)$$

If, however, the Al is carburized through a solid-phase reaction with the graphitic-like carbon, then the following reaction is expected:

$$4Al(s) + 3C(s) \rightarrow Al_4C_3(s) \quad (2)$$

Reaction (2) should not affect the weight loss since only solid phases are involved in the reaction. In reaction (1), the carbon in the gas phase, which would normally be lost to the atmosphere if the Al particles were not present, would now be retained in the body, resulting in a smaller weight loss during pyrolysis than that without Al. This would imply that reactions (1) and (2) both contribute to the carburization of Al.

When the pyrolysis temperature was elevated to 800 °C, AlN diffraction peaks were observed (Fig. 3), which corresponds well with the result of thermal analysis. It can be found from Fig. 3 that crystalline Si phase was present, implying that the Si–O–C matrix phase may be

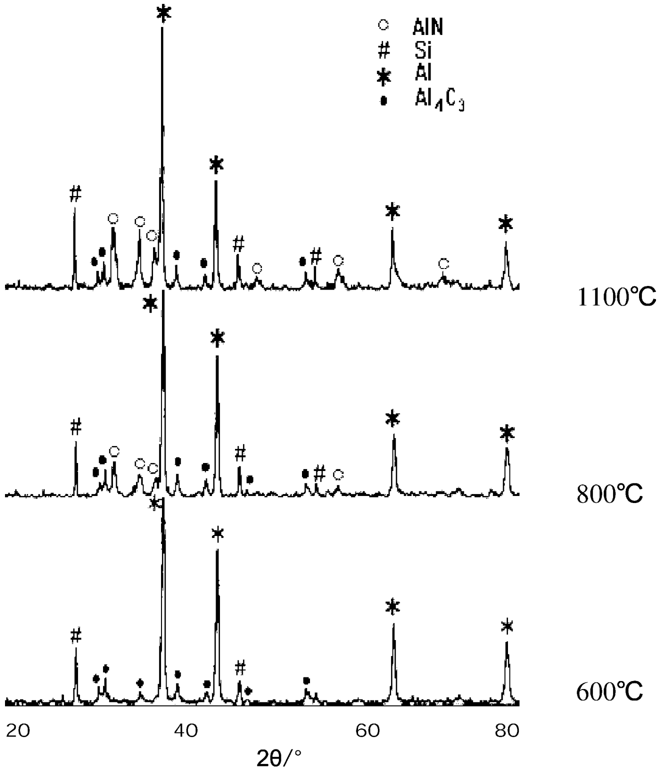

Fig. 3. XRD patterns of pyrolysates of Al-filled PSO/DVB at different temperatures.

Table 3
Densities and properties of Al-containing SiC/Si–O–C composites with various content of Al

Sample	Content of Al powders (vol.%)	Density (g/cm^3)	Linear shrinkage (%)	Flexural strength at room temperature (MPa)
A0	0	2.103	13.0	142.9
A10	10	–	7.9	–
A20	20	2.255	5.7	193.9
A30	30	2.363	5.0	94.3

Remark: Content of Al powders was referred to as the volume ratio of Al powders to (PSO + DVB).

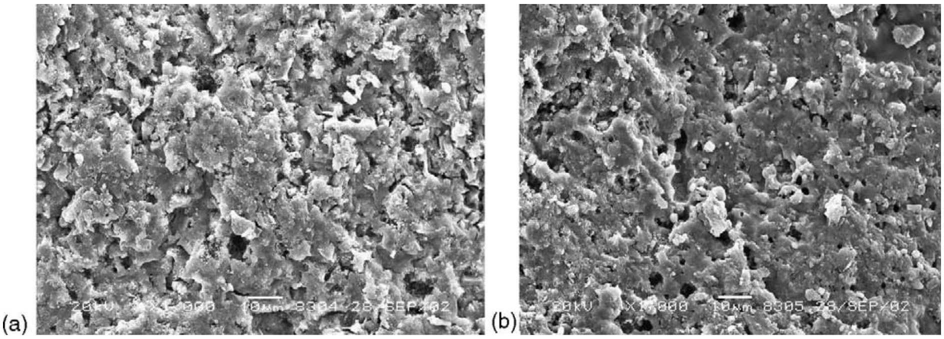

Fig. 4. SEM photos of fracture surface of sample A20 (a) and A30 (b).

reduced in the presence of Al. Further research involving thermodynamic calculations and kinetic studies is necessary to thoroughly interpret the result.

3.3. Properties of Al-containing SiC/Si–O–C composites

Earlier work showed that such slurries sediment very quickly as a result of the large particle size of active fillers [11], which can result in stresses due to an inhomogeneous polymer pyrolysis. In order to prevent the sedimentation of Al fillers in PSO/DVB and stabilize the suspension, SiC powders were used. Prior to the addition of Al fillers, 17.2 vol.% SiC powders were dispersed into PSO/DVB solution, followed by the addition of various content of Al fillers.

Table 3 shows the densities and properties of Al-containing SiC/Si–O–C composites with various content of Al powders. As expected, adding Al fillers reduces the shrinkage of 40 wt.% SiC/Si–O–C composites, which was ascribed to the Al filler volume effect and the volume expansions resulting from the reactions of Al and free carbon (+9%), Al and hydrocarbons (+53%) and Al and nitrogen (+26%) [12]. The flexural strength of sample A20 reached 193.9 MPa, which is 1.36 times that of sample A0. This could be attributed to three causes. Firstly, the porosity was decreased by the volume expansion, and then the composites became more compact. Secondly, the unreacted Al fillers and the created Al_4C_3 and AlN could deflect crack or stop crack extending. Thirdly, the unreacted Al melted above 660 °C and penetrated into pores, hence increased the bonding of fillers. The fact that the flexural strength of sample A30 is inferior to that of sample A20 may be due to the looser microstructure (as shown in Fig. 4), which needs further investigation.

The oxidation resistance, thermal shock resistance and high temperature resistance of sample A20 and A30 were characterized by the same methods as those for SiC/Si–O–C composites, and the results are presented in Table 4. Compared with the values in Table 2, it can be noted that the addition of Al remarkably increases the high temperature resistance and oxidation resistance of SiC/Si–O–C composites. As mentioned above, the decomposition of Si–O–C matrix occurred when heated at 1500 °C for 2 h under an atmosphere of nitrogen, resulting in pores in composites. At the same time, the reaction between the unreacted Al and N_2 also occurred during heat treatment, creating AlN accompanied with volume expansion. The pores due to the decomposition of Si–O–C matrix would be eliminated by

Table 4
Oxidation, thermal shock and high temperature resistances of Al-containing SiC/Si–O–C composites

Content of Al fillers (vol.%)	Flexural strength (MPa)					
	Oxidation resistance		Thermal shock resistance		High-temperature resistance	
	Before	After	Before	After	Before	After
20	193.9	167.1	193.9	49.3	193.9	157.3
30	94.3	125.7	94.3	–	94.3	91.7

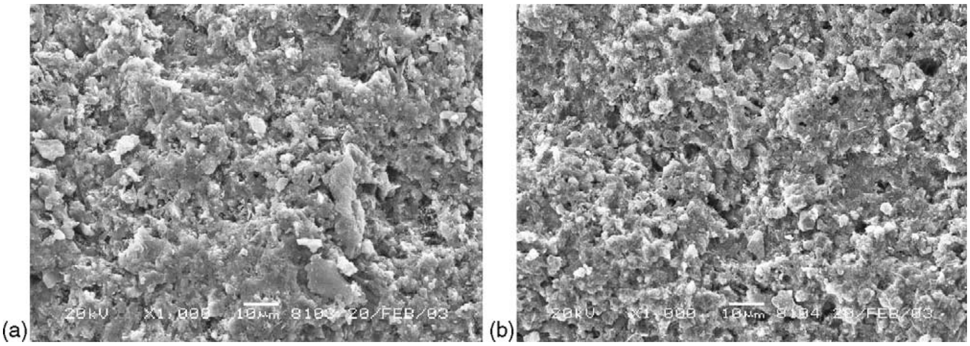

Fig. 5. SEM photos of fracture surface of sample A20 (a) and A30 (b) after heated under N_2 at 1500 °C for 2 h.

the volume expansion. Then, the densities of sample A20 and A30 did not decrease. Fig. 5 shows the fracture surfaces of sample A20 and A30 after heating under nitrogen at 1500 °C for 2 h. Compared with Fig. 4, it appears that the microstructures of sample A20 and A30 before and after heat treatment are almost the same, demonstrating that heat treatment did not decrease the density of the composites. As a result, Al-containing SiC/Si–O–C composites exhibited excellent high temperature resistance. Sample A20 and A30 possessed 81.1% and 97.3% of their original flexural strengths after heat treatment, respectively.

When oxidized under static air at 1100 °C for 10 h, free carbon in composites was oxidized and many pores were created. At the same time, the unreacted Al fillers were also oxidized, creating Al_2O_3 with +28% specific volume expansion [13]. This expansion could compensate the pores resulting from the oxidation of free carbon and the created Al_2O_3 could act as reinforcement. Accordingly, sample A20 and A30 exhibited excellent oxidation resistance. Sample A20 and A30 possessed 86.2% and 133.3% of their original flexural strengths after oxidation, respectively.

A possible explanation for the better high temperature resistance and oxidation resistance of sample A30 with respect to sample A20 was that more total volume expansions were created because there were more Al fillers in sample A30 reacting with N_2 or O_2.

However, sample A20 retained only 25.4% of its original flexural strength after thermal shock, indicating that the addition of Al does not improve the thermal shock resistance of SiC/Si–O–C composites. The mismatch of thermal expansion coefficients between Al, SiC and Si–O–C matrix was suggested being responsible for the poor thermal shock resistance of Al-containing SiC/Si–O–C composites.

4. Conclusions

Based on the results of this study, the following generalized conclusions can be drawn:

(1) Adding SiC fillers into PSO/DVB solution reduces the linear shrinkage of filler-free cured PSO/DVB and yields monolithic SiC/Si–O–C composites. At the same time, SiC filler is an effective reinforcement. The flexural strength of SiC/Si–O–C composites reaches 201.3 MPa at a SiC filler content of 27.6 vol.%. However, SiC/Si–O–C composites exhibit poor oxidation, thermal shock and high temperature resistances.

(2) Al fillers is supposed to react with hydrocarbon generated during PSO/DVB pyrolysis at 600 °C to create Al_4C_3 as well as volume expansion. At 800 °C, Al fillers react with nitrogen to form AlN as well as volume expansion.

(3) The flexural strength of Al-containing SiC/Si–O–C composites is 1.36 times that of SiC/Si–O–C composites without Al at an Al filler content of 20 vol.%.

(4) The addition of Al fillers remarkably improves the high temperature resistance and oxidation resistance of SiC/Si–O–C composites, but not their thermal shock resistance.

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