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Liquid poly(silylacetylene)siloxane resin as a novel precursor of silicon carbide and silicon oxycarbide ceramics

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Abstract

Liquid preceramic poly(silylacetylene)siloxane resin was synthesized via a two-step protocol including organometallic condensation and hydrolysis reactions. The preceramic resin was well soluble in acetone, toluene, and tetrahydrofuran (THF), etc. By thermal cure at 180–250 °C a hard monolithic solid was formed through radical polymerization of secondary ethynyl groups. The poly(silylacetylene)siloxane resin was processed easily to various nonporous shapes to silicon carbide (SiC) and silicon oxycarbide (SiCO). SiCO ceramic was obtained at a yield of >75% by pressureless pyrolysis at 900–1200 °C; while SiC ceramic was obtained at 1500 °C at a yield of ≈67%. The molar ratio of Si/C in the SiC was found at 1:1.1–1:3, based on ICP-MS elemental analysis. X-ray diffraction (XRD) results revealed the typical β-SiC structure in the poly(silylacetylene)siloxane derived SiC ceramics. The SiC ceramics exhibited high thermo-oxidation resistance at elevated temperatures in air atmosphere.

Keywords: Precursor; Resin; Cure; Ceramics

1. Introduction

Advanced non-oxide ceramics such as silicon carbide (SiC) are attracting gradually growing interest in the application as high performance materials [1]. SiC monolithic materials can be fabricated by a variety of techniques such as powder sintering, sol–gel, chemical vapor deposition and polymer conversion [2]. Silicon-based polymers have proven to be promising precursors for the production of advanced ceramic components [3]. The most competitive advantage of polymer precursors is that their ideal solubility or fusibility allows the shaping to be carried out at moderate temperatures and by conventional polymer processing techniques for the production of various complex shapes such as fibres, coatings and bulk bodies [4].

Polycarbosilane (PCS) resin was studied as the most successful SiC precursor for over 35 years [5]. A variety of polycarbosilanes were reported by Yajima [6]. Wurtz coupling reaction combined with high temperature Kumada rearrangement was a synthesis method for PCS initiated by Yajima et al. [7]. Although Yajima type PCS resins have been widely studied and applied [8], the Yajima PCS encountered unavoidable drawbacks such as high synthetic cost, low fluidability, foamable cure and low ceramic yield [9].

New synthetic methods are highly appreciated for SiC preceramic resins. Ideal preceramic resins are expected to have low cure temperatures (<300 °C), high ceramic yields (>70%), high purity (near stoichiometric elemental ratio, meaning high thermal stability), and ease of use (viscous liquid at RT with ideal rheology for material processing). Several silicon-containing resins have been studied as high efficient SiC precursors. STARFIRE® SMP-10 by Starfire Systems Company is the only commercially available one-component liquid precursor for SiC [10]. SPM-10 was reported to be synthesized via Grignard coupling reaction of mixed chlorosilanes [11]. The

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Griganrd reaction between chlorosilane and dibromomethane was reported to obtain a liquid polycarbosilane [12]. Additionally, a kind of hyperbranched PCS with unsaturated curable groups (ally, propargyl or ethynyl) was widely studied, but its synthetic cost was too high [13]. Polysilane was also under investigation as SiC precursor, although it is unstable upon storage owing to its sensibility to light and oxygen [14]. The precursor by sol–gel chemistry and thermocarbon reduction was also studied widely, but its applications were limited in polymer derived ceramics and ceramic composites [15].

Facile and cost-efficient synthetic methods for polycarbosilanes is promising, and attracting a lot of research interests in both academia and industries. In this paper, a novel poly(silylacetylene)siloxane resin was synthesized and converted to nonporous SiC and SiCO monoliths via thermal cure and thermal carboreduction. The results revealed that the poly(silylacetylene)siloxane resin is a promising polymer precursor for the fibre and ceramic composite matrix of silicon carbide or silicon oxycarbide.

2. Experimental

2.1. Materials

Trichloroethylene, methyldichlorosilane and n-BuLi (2.5 M in n-hexane) were all purchased from Fluka, and used as received. The deionized water was from Institute of Microelectronics of the Chinese Academy of Sciences.

2.2. Synthesis of poly(silylacetylene)siloxane resin [16]

A 3-neck glass flask was dried and purged with nitrogen gas, and n-BuLi (100 mL, 0.25 mol; 2.5 M in n-hexane) was charged into the flask via syringe. When cooled to −50 °C, trichloroethylene (0.08 mol, 10.52 g) was added dropwise to avoid rapid temperature increase. Then methyldichlorosilane (0.16 mol, 18.4 g) was added and aged for 2 h. At last, deionized water (0.5 mol, 9 g) was added. After the salt was infiltrated, the filtrate was evaporated to give a brown viscous resin, followed by purifying via hot water rinsing to obtain the final resin products.

2.3. Thermal cure of poly(silylacetylene)siloxane resin

The poly(silylacetylene)siloxane was cured in a vacuum oven according to the following procedure: @ 120 °C for 1 h, @ 160 °C for 1 h, @ 210 °C for 2 h and @ 250 °C for 2 h. After the thermal cure, the poly(silylacetylene)siloxane was converted into a dark red brittle nonporous monolith.

2.4. Pyrolysis of the cured precursor

The pyrolysis was conducted in a tube furnace under Ar atmosphere as per the following heating schedule: room temperature (RT) to 250 °C at 10 °C/min; 250–600 °C at 3 °C/min; @ 600 °C for 1 h; 600–900 °C (1200 °C and 1500 °C, respectively) at 5 °C/min and @ 900 °C for 2 h. After the pyrolysis, grey hard ceramic solids without visible pores were obtained.

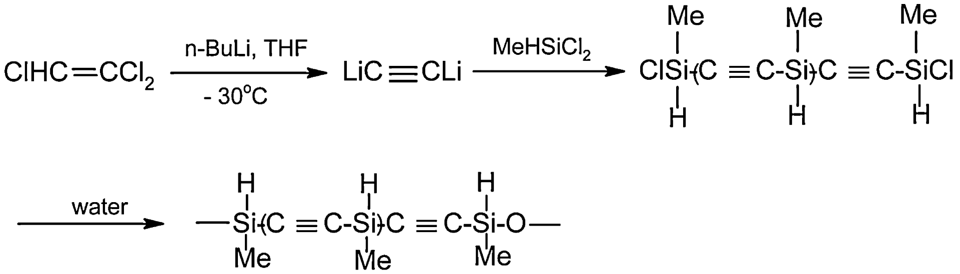
2.5. Characterizations

The Gel Permeation Chromatography (GPC) was recorded on Waters 1515 GPC instrument (Refraction Index Detector 2414), using THF as eluent at 1 mL/min and polystyrene standards for calibration. FT-IR spectra were obtained over the range of 4000–400 cm^{-1} using a Perkin Elmer System 2000 spectrometer. ^{1}H NMR was recorded on Bruker 400 using $CDCl_3$ as the solvent. Viscosity was monitored with a Rotary Viscometer NDJ-1. Differential Scanning Calorimetry (DSC) analysis was conducted on a Mettler-Toledo DSC1 in N_2 atmosphere at a heating rate of 10 °C/min. Thermogravimetric Analysis (TGA) was studied on NETZSCH STA 409pc in N_2 atmosphere at 10 °C/min heating rate. X-ray diffraction (XRD) was conducted using a Shimadzu XRD-7000s. The elemental analysis was performed by the technique of ICP-MS on Agilent 7500a. Scanning Electron Microscope (SEM) measurements were made on a Hitachi S-4800 scanning electron microscope integrated with an Energy Dispersive X-ray Spectrometer (EDX). The densities of preceramic resin, cured resin and ceramic residues were determined at 25 °C by the pyconometer method using water as the reference.

3. Results and discussion

3.1. Synthesis and structure characterizations of poly(silylacetylene)siloxane

The synthetic protocol of poly(silylacetylene)siloxane resin was based on two-step reactions: the condensation of dilithium acetylide and methylchlorosilane, and the hydrolysis of the terminated silylchloride, as shown in Scheme 1. The synthesis



Scheme 1. Synthetic protocol of poly(silylacetylene)siloxane resin.

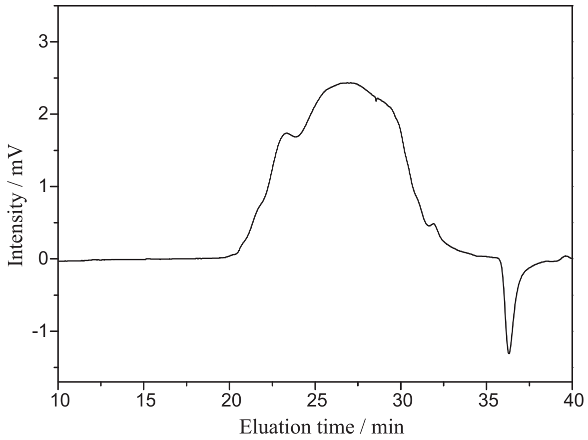


Fig. 1. GPC profile of poly(silylacetylene)siloxane resin (THF eluent, 1 mL/min).

should be conducted by Schlenk technique so as to avoid the destructive reactions of moisture and oxygen [17]. The reactions in this protocol are easily controlled, and the resin is obtained with a high yield of >90%.

The poly(silylacetylene)siloxane resin was successfully prepared on a large scale of 5 kg, so it is a promising precursor for SiC and SiCO s that has found a wide range of industry applications [18].

As shown in Fig. 1, the M_n of the poly(silylacetylene)siloxane resin is about 1000 g/mol, M_w is about 2100 g/mol, and the ID (index of polydispersity) is 2.1. The broad distribution of the molecular weights revealed the characteristics of condensation resins like phenolic and epoxy resins. So the poly(silylacetylene)siloxane resin had excellent processing capability, e.g. good solubility in acetone, suitable viscosity (500 mPa s at 25 °C) and a wide thermal processing window (from RT to 220 °C, determined by DSC analysis). The ideal rheological property is of high importance to process the poly(silylacetylene)siloxane resin into required shapes.

The molecular characteristics are similar when the length of the silylacetylene segment varies, but the oxygen content (in siloxane bonds) should be monitored to guarantee the successful proceeding of carbothermal reduction and the occurrence of the designed ceramic structure.

The molecular structure was characterized by FT-IR and ^{1}H NMR, as shown in Fig. 2. In FT-IR spectrum, the absorption at 2049 cm^{-1} can be attributed to C≡C stretching vibration, 1251 cm^{-1} is attributed to Si–Me vibration and 1060 cm^{-1} to Si–O vibration. The information in ^{1}H NMR spectrum is in good agreement with the FT-IR results: the peak at 4.1–4.4 ppm is from Si–$\underline{\mathrm{H}}$, while the peak at 0.45–0.7 ppm is from Si–C$\underline{\mathrm{H}}_3$.

3.2. Thermal properties

Upon heating, the free-radical addition polymerization of ethynyl groups in poly(silylacetylene)siloxane resin could proceed readily to form a brittle and hard monolithic material. As shown in Fig. 3 (DSC spectra of poly(silylacetylene)siloxane resin (10 °C/min, N_2 at 50 mL/min)), the thermal cross-linking reaction of poly(silylacetylene)siloxane resin initiated at about 240 °C, peaked at about 300 °C and ended at about 360 °C. After complete thermal cure, the density of the cured poly(silylacetylene)siloxane resin is increased from original 0.9 to 1.1 g/cm^3. The thermal curability imparted the poly(silylacetylene)siloxane resin with excellent processing capability – a property which the PCS does not have, which makes it possible of making nonporous materials with diverse shapes.

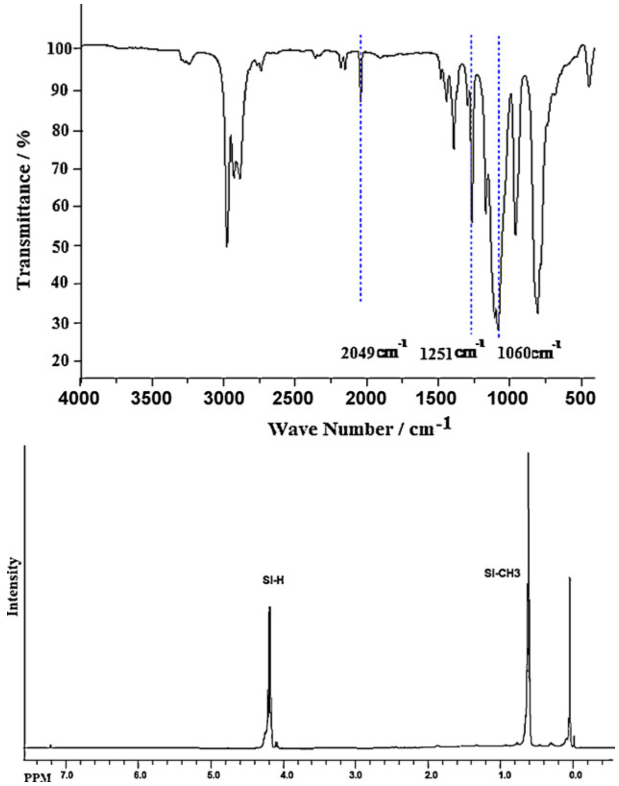


Fig. 2. FT-IR and ^{1}H NMR spectra of poly(silylacetylene)siloxane resin.

The rheology upon heating was monitored by acquiring the viscosity at different temperatures, and the results were shown in Fig. 4. It can be revealed that the poly(silylacetylene)siloxane resin has a broad processing window in the range of RT to 200 °C, and the viscosity measured was ideal (low and stable) for the ceramic composite materials' fabrication.

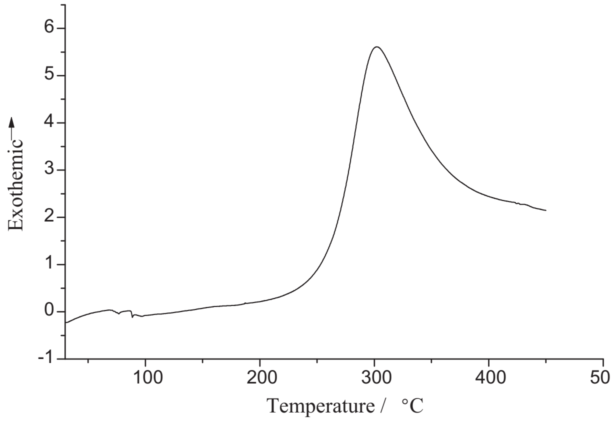


Fig. 3. DSC graph of poly(silylacetylene)siloxane resin (10 °C/min, N_2 at 50 mL/min).

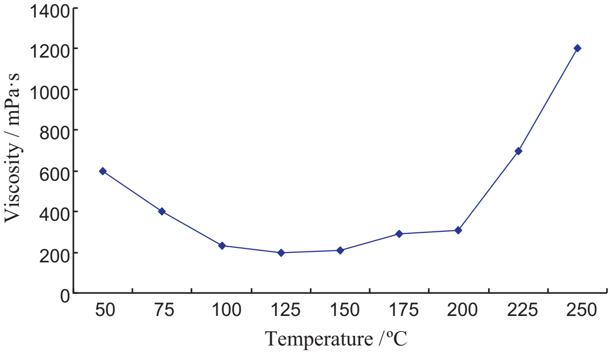


Fig. 4. The viscosity–temperature relationship profile of poly(silylacetylene)-siloxane resin.

The cured poly(silylacetylene)siloxane resin could be further converted to hard ceramics in inert gas atmosphere (Ar or N_2). As shown in Fig. 5, the thermal decomposition started at 480 °C, ended at about 800 °C, and yielded a residue at 86 wt%. The residue basically contains silicon, oxygen and carbon; with increasing the temperature to 1500 °C, thermocarbon reduction will occur for the conformation of Si–O–C to SiC, accompanied with a mass loss of about 20% (the results from practical pyrolysis in furnace).

3.3. Pyrolysis to SiC ceramics

Pressureless pyrolysis at low temperatures (compared with the powder sintering process where the sintering temperature is normally as high as >1800 °C) is the most attractive advantage for polymer-derived ceramics. In this paper, the poly(silylacetylene)siloxane resin was pyrolyzed in a tube furnace at 900, 1200 and 1500 °C, respectively. The final residues were hard grey monolithic solids with no visible pores.

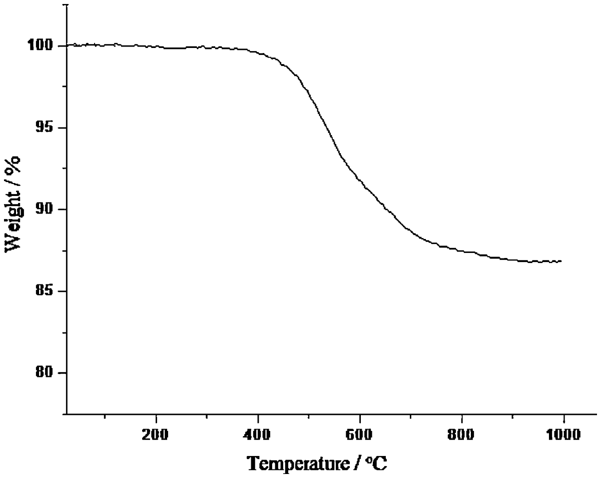


Fig. 5. TGA graph of the cured poly(silylacetylene)siloxane resin (10 °C/min, N_2 at 50 mL/min).

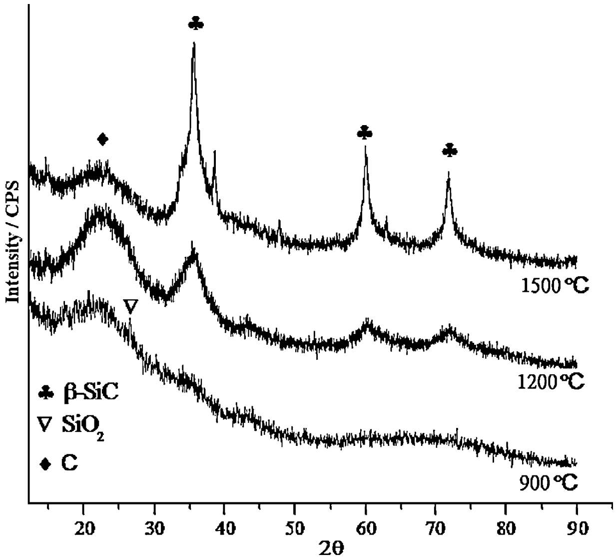


Fig. 6. XRD graph of poly(silylacetylene)siloxane derived ceramics.

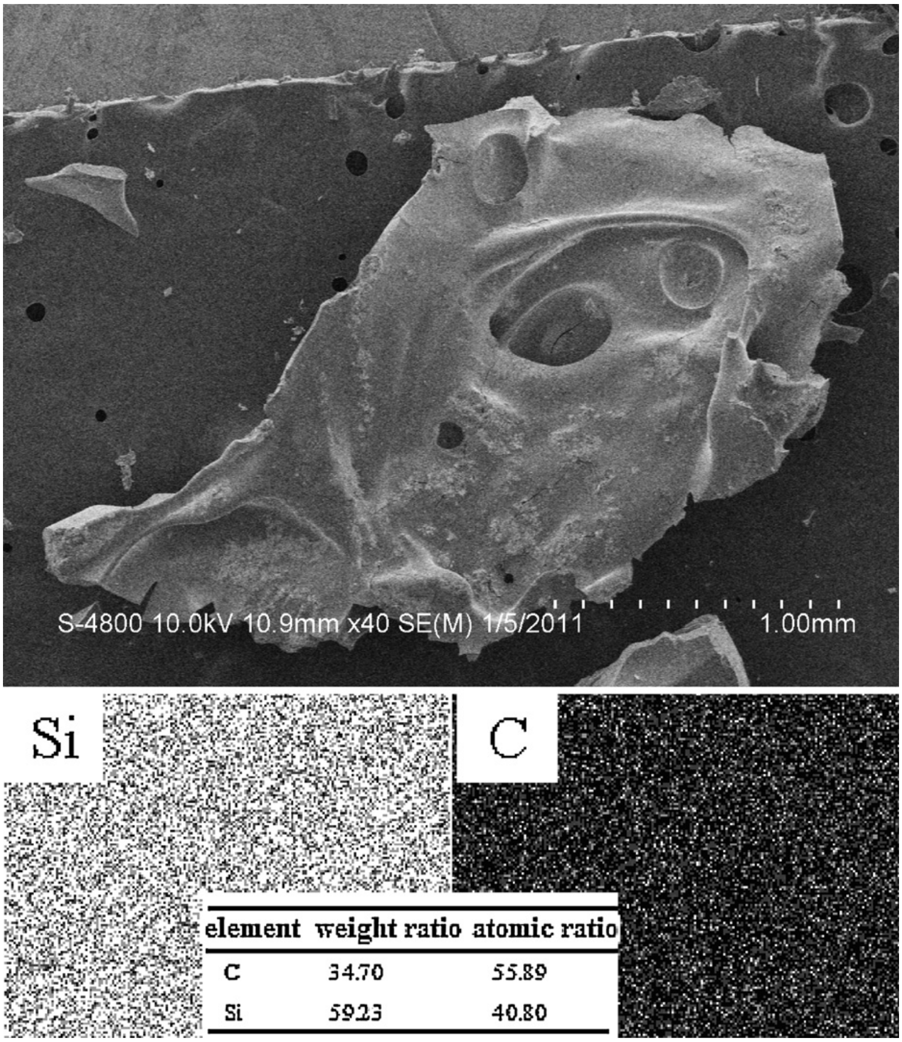
X-ray diffraction (XRD) was recorded to reveal the crystal structures of the ceramic residues, as showed in Fig. 6. Obviously, the pyrolysis at 900 °C only led to an amorphous ceramic. 1200 °C was still insufficient for a complete thermocarbon reduction (viz. the thorough conformation to SiC), but the pyrolysis at 1500 °C led to the formation of well-defined β-SiC. The above results could be also implied by the residue yields: 82 wt%, 75 wt% and 67 wt% at 900 °C, 1200 °C and 1500 °C, respectively. The gradual decrease of residue yields means the proceeding of thermocarbon reduction and oxygen elimination. Meanwhile, the change of the densities were also in good agreement with the above results: at 900 °C, the residue with a density of 2.1 g/cm^3; at 1200 °C, the residue with a density of 2.4 g/cm^3; at 1200 °C, the residue with a density of 3.0 g/cm^3. The gradual increase of the density of the ceramic residue implies the gradual proceeding of the conversion.

The elemental analysis was used to determine the formula of the resulted ceramic residues, and the results are showed in Fig. 7 and Table 1. Evidenced by the ICP-MS data in Table 1, with the 1200 °C pyrolysis, the ceramic residue has a lot of unwanted carbon, and the content of Si + C is at a low level of 70 wt% (the remaining 30 wt% is oxygen). These results are in accordance with the XRD analysis. At 900–1200 °C, silicon oxycarbide ceramics were formed. At 1500 °C, the ceramic showed a high content of Si + C of 97.2 wt%, indicating the nearly complete elimination of oxygen and the formation of comparable pure SiC. As shown in Fig. 7 of SEM-EDS, the ceramic residue is a nonporous monolith with a Si/C ratio of 1:1.36.

It should be noted that, for the conventional polycarbosilane resin (a widely used precursor for SiC), only foam-like solid ceramics were obtained upon thermal pyrolysis. In this work, owing to its good thermal curability and ideal rheology, the

Table 1
Elemental analysis results of poly(silylacetylene)siloxane derived ceramics.

Ceramic samples	C (wt%)	Si (wt%)	Empirical formula
1200 °C pyrolysis	34.2	36.5	$Si_{1.0}C_{2.19}$
1500 °C pyrolysis	36.0	61.2	$Si_{1.0}C_{1.37}$



element	weight ratio	atomic ratio
C	34.70	55.89
Si	5923	40.80

Fig. 7. SEM-EDS results of poly(silylacetylene)siloxane derived ceramic at 1500 °C.

poly(silylacetylene)siloxane resin can be converted to nonporous monoliths at a high yield.

4. Conclusions

Poly(silylacetylene)siloxane resin was prepared as a polymeric precursor for the production of silicon carbide and silicon oxycarbide. The molecular structure was confirmed by FT-IR and GPC. Upon heating, the curing polymerization of poly(silylacetylene)siloxane resin could proceed smoothly to form a brittle monolithic solid. The pressureless pyrolysis of the poly(silylacetylene)siloxane resin produced SiCO at 1200 °C, but SiC at 1500 °C at a yield of ≈67%. The formation of β-SiC was ascertained by the measurements of XRD and elemental analysis. The research demonstrates a new promising way to produce advanced nonporous monolithic SiC and SiCO ceramics.

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