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Oxidation Behavior of a Fully Dense Polymer-Derived Amorphous Silicon Carbonitride Ceramic

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The oxidation behavior of a polymer-derived amorphous silicon carbonitride (SiCN) ceramic was studied at temperature range of 900°–1200°C using fully dense samples, which were obtained using a novel pressure-assisted pyrolysis technique. The oxidation kinetics was investigated by measuring the thickness of oxide layers. The data were found to fit a typical parabolic kinetics. The measured oxidation rate constant and activation energy of the SiCN are close to those of CVD and single-crystal SiC. The results suggest that the oxidation mechanism of the SiCN is the same as that of SiC: oxygen diffusion through a silica layer.

I. Introduction

SILICON-BASED covalent ceramics can be alternatively synthesized by thermal decomposition of polymer precursors,[1] called polymer-derived ceramics (PDCs). Figure 1 shows the basic processing steps of PDCs:[2] (i) synthesis of polymer precursor from proper starting chemicals, (ii) cross-linking of precursor to form preceramic network structure, and (iii) conversion to ceramics by pyrolysis at ~1100°C. The resultant materials are amorphous alloys of silicon, carbon, and nitrogen (SiCN); other elements such as boron can also be incorporated into the network to modify and improve properties.[3] Whereas the polymer precursor route has been known since the mid 1970s,[4] the new generation of PDCs focuses on tailoring the compositions/structures of the ceramics through designing the chemistry of precursors.[2] Compared with conventional powder-based processing for silicon-based ceramics, this unique chemical-to-ceramic technique possesses many advantages, for example:

(1)   The technique leads to a flexible and relatively cost-efficient approach to manufacture ceramic components and devices. Complex shapes can be made in the organic form with techniques developed for polymer forming, just before pyrolysis, which will yield self-similar ceramic components and devices. The fabrication of high-temperature fibers,[4,5] protective coatings,[6] ceramic matrix composites,[7,8] ceramic micro-electro-mechanical systems (MEMS),[9–13] and, most recently, SiC/Si$_3$N$_4$ nanorods and nanobelts[14,15] has been demonstrated.

(2)   It offers a unique opportunity to manipulate the structure and composition, and thereby the properties, of ceramics by designing the chemistry of the polymer precursors.

When synthesized at relatively low temperatures, some PDCs possess a set of excellent thermo-mechanical properties at ultra-high temperatures. For example, boron-contained SiCN (SiBCN) ceramics resist crystallization and thermal decomposition at temperatures up to 2000°C.[3,16] Creep studies[17–19] indicated that some amorphous PDCs exhibited "creep hardening" behavior—the creep rate decreases with time, similar to metallic glasses.[20,21] The creep rate of the SiBCN is even lower than that of state-of-the-art polycrystalline Si$_3$N$_4$ at temperatures >1500°C.[18] The PDCs also possess high hardness and fracture strength at room temperature.[22] Because of the absence of grain-boundary phases, which resulted from sintering additives, it is expected that such excellent mechanical behavior can be retained at high temperatures. Consequently, PDCs are very attractive in the design of next generation ultrahigh-temperature structural materials.

When considering silicon-based materials for high-temperature applications, oxidation becomes a critical issue. The oxidation behavior of ceramics derived from chemical precursors has been the subject of a few previous studies. Bahloul *et al.*[23] performed the oxidation studies on SiCN ceramics obtained from different pyrolysis conditions, leading to different carbon content or presence of the same amount of carbon in different forms (free carbon or mixed tetrahedra). They concluded that the combustion of free carbon initiates the oxidation of SiCN, facilitated by the oxygen diffusion through the microporosity created. The SiCN exhibits similar oxidation behavior as SiC and Si$_3$N$_4$ once the free carbon is burned out. Mocaer *et al.*[24] studied the oxidation kinetics of the SiCN filaments. They found the parabolic rate constants lower than those observed for SiC but higher than those for Si$_3$N$_4$. The calculated activation energy was 170 kJ/mol, comparable to those obtained for SiC. Recently, the oxidation kinetics of a SiCN ceramic was measured at 1350°C.[25] The results indicated that the oxidation of the SiCN can be classified into short-term and long-term regions. In short-term, the oxidation is caused by the growth of silica films on the inner surfaces of nano-pores, resulting in weight gain saturated exponentially with time. In long-term, the
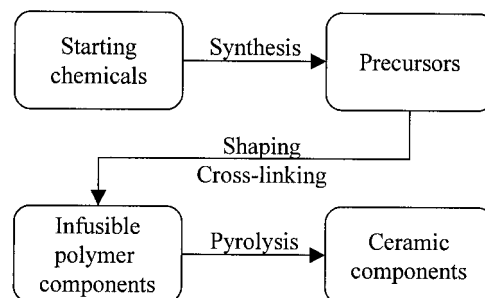
Fig. 1.   Flow chart showing the basic processing steps of polymer-derived ceramics.

oxidation is from the growth of a silica layer on the surface of the sample, resulting in parabolic behavior. All the above mentioned studies were conducted by measuring weight change. The thickness of the oxide layer as a function of time has been measured in polymer-derived SiBCN ceramics at 1300° and 1500°C.[26] The results suggested that the SiBCN possesses slightly better oxidation resistance than CVD SiC.

In this paper, we report studies on the oxidation behavior of a fully dense SiCN ceramic derived from a polyurea(methylvinyl)-silazane, which is liquid at room temperature and has been used to fabricate MEMS for severe environmental applications.[9–13] The fully dense disk samples were obtained using a novel pressure-assist pyrolysis technique. The oxidation kinetics was studied by measuring the thickness of oxide layer as a function of time at the temperature range of 900°–1200°C. The results revealed that the growth of oxide scale follows parabolic kinetics with the rate constant in the same range as that of high-purity polycrystalline SiC and Si_3N_4 ceramics. The oxidation activation energy measured is 120 kJ/mol, which is close to that for single-crystal silicon and CVD SiC. The present results suggest that the oxidation of the polymer-derived SiCN is similar to that of SiC: the rate control mechanism is the oxygen diffusion through the silica layer.

II. Experimental Procedures

(1) Material Preparation

Commercialy available polyurea(methylvinyl)silazanes (Cera-set[SN], Kion, Huntingdon Valley, PA) was used as the starting precursor. The thermal decomposition processes of Ceraset were reported previously.[27] In the present study, fully dense disk-shaped samples were prepared using a novel pressure-assisted pyrolysis technique, as described by An *et al.*[9] and followed by others.[10–13,22] The liquid mixture of Ceraset with 2–4 wt% dicumyl peroxide (Acros Organics, Morris Plains, NJ) initiator was first placed in a Teflon tube of 0.5-inch inner diameter and then solidified by heat-treating at 150°C for 0.3 h. Such formed solid polymer rod was transparent and easy to remove from the tube. The rod was then cross-linked at 400°C under isostatic pressure, which effectively suppressed the formation of bubbles and cracks otherwise formed at this stage.[9,27] The cross-linked rod remained transparent, indicating the absence of defects. Next, the disks of 2–3-mm thickness were cut from the rod and pyrolysized at 1100°C under isostatic pressure. Amorphous SiCN ceramic disks were then obtained. To examine the microstructure of the obtained ceramics, the cross section of the obtained ceramics was polished to a 0.5-μm finish and observed under scanning electron microscopy (SEM).

The composition of the obtained disks was measured with conventional elemental analysis; the apparent composition is $SiC_{0.99}N_{0.85}$. The ceramics also contain ~3 wt% oxygen. The carbon content is slightly higher than that reported previously,[27] possibly from the addition of the initiator or the applied pressure that partially prevents the evaporation of carbon-containing pyrolysis by-products.

(2) Oxidation Study

In this section, we will discuss the oxidation studies performed on the disks obtained from the prior section. First, one surface of each disk was polished to 0.5-μm finish using diamond-lapping film. The sample was then loaded in a high-purity silica glass tube to prevent potential contamination from the alumina working tube and placed in a high-temperature tube furnace (Thermolyne, Dubuque, IA) with the polished surface face up. The oxidation studies were conducted in air at temperatures of 900°, 1000°, 1100°, and 1200°C for 20, 50, 100, and 200 h each. The heating and cooling rates of 25°C/min were used.

After oxidation, the polished surface was first examined under SEM to check the integrity of the oxide layer. To closely observe the morphology and measure the thickness of the oxide layer, the cross section of the oxidized disk was observed using SEM. First, the surface of the disk, which was polished before oxidation, was coated with a 0.2–0.5-μm-thick chromium layer using a precision etching coating system (PECS, Gatan, Inc., Pleasanton, CA) to protect the oxide layer from potential damage during polishing. The cross section of the samples was then polished to a 0.5-μm finish. The polished cross section was then etched using buffered oxide etchants (BOE, Ashland Chemical, Boonton, NJ) to delineate the oxide layer from the ceramic substrate. The cross section was then coated with gold–palladium and observed under SEM. The thickness of the oxide layers was measured using SEM micrographs. For each sample, at least three measurements were taken; and it was found that the values from different measurement of the same sample did not differ by much.

III. Results and Discussion

It was previously demonstrated[9,22] that the fully dense SiCN ceramics can be obtained by the thermal decomposition of the Ceraset precursor with the pressure-assisted pyrolysis technique. In this work, a similar processing was followed, except that the isostatic pressure was applied during pyrolysis to further improve the quality of the samples. The ceramic disk obtained is black, as shown in Fig. 2(a). The diameter of the ceramic disk is ~9 mm, corresponding to ~30% linear shrinkage compared with that (12.5 mm) of polymer disks just solidified. Figure 2(b) is a SEM micrograph showing a typical microstructure of the SiCN ceramics. Note that the micrograph is featureless at this scale, indicating there are no detectable defects in the ceramic. The density of the obtained ceramics was measured with Archimedes principle to be 2.23 g/cm³, which is similar to that of the powder obtained by crushing the bulk samples, confirming the samples are fully dense.

The observation of the oxidized surfaces revealed that no bubbles and cracks were formed for most samples, with the
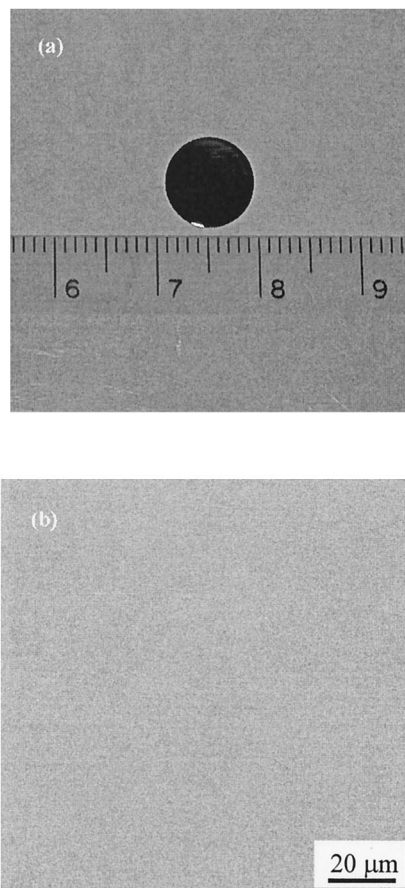
Fig. 2. (a) Optical micrograph showing the SiCN ceramic disk 9 mm in diameter and 2 mm thick; (b) SEM micrograph showing the microstructure of SiCN ceramic. **Note**: there are no detectable defects.
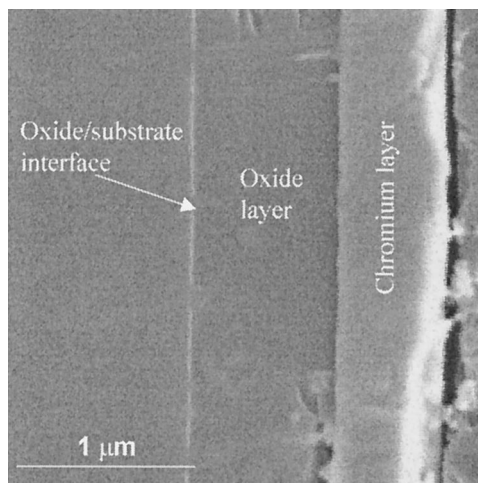
Fig. 3. SEM micrograph of the cross section of a SiCN disk oxidized at 1200°C for 50 h. **Note**: a fully dense oxide layer with uniform thickness was formed on the surface of the sample.

exception of those oxidized at 1200°C for >100 h. In these cases, some cracks were formed on the surface, although there was no spallation. Figure 3 is a typical SEM micrograph of the cross section of the oxidized samples. It can be seen that the oxide/ceramic substrate interface was clearly delineated by the etching, which makes the measurement of the thickness of the oxide layer much easier. A fully dense oxide layer with uniform thickness and a good adhesion to the ceramic substrate was observed from every sample.

The thickness of the oxide layer at different oxidation conditions (temperatures and times) were measured from SEM micrographs. Figure 4 is a plot of the square of the thickness of the oxide layer as a function of annealing time for different testing temperatures. Each data point represents the average of at least three measurements. It can be seen that the growth of the oxide layer fits a typical parabolic kinetics:

$$h^2 = k_p t \qquad (1)$$

where h is the thickness of the oxide layer, t the annealing time, and k_p the parabolic rate constant. The rate constants at different temperatures were calculated and are listed in Table I. These values lie in between those for CVD SiC[28–30] and single crystalline silicon,[31] but are higher than that of CVD Si_3N_4.[28,30,32–34]

Table I. Parabolic Rate Constant for the SiCN Ceramic from 900°–1200°C

	900°C	1000°C	1100°C	1200°C
$k_p \times 10^{-18}$ (m²/sec)	0.39	1.3	2.8	4.8

The apparent activation energy of the oxidation can be measured from the rate constants of the different temperatures according to Arrhenius equation:

$$k_p = A_o \exp\left(-\frac{Q_A}{RT}\right) \qquad (2)$$

where Q_A is oxidation activation energy. Figure 5 plots the log (parabolic rate constant) against reciprocal temperatures. A fairly good linear relation is obtained, indicating a single oxidation mechanism in the testing temperature range. The slope of the straight line in Fig. 5 is $-Q_A/R$. The calculated activation energy calculated is 120 kJ/mol. The activation energy value is close to that of high-purity SiC (such as CVD and/or single-crystal SiC)[28–30] and single-crystal silicon,[31] but much less than that of CVD silicon nitride.[28,30,32–34] This suggests that the oxidation mechanism of the SiCN is similar to that of SiC: oxygen diffusion through the silica layer. This result also suggests that the nitrogen has no effect on the oxidation behavior in this particular SiCN ceramics in the testing temperature range.

Finally, we will discuss the two techniques used to measure the oxidation kinetics of polymer-derived ceramics: weight change and thickness measurement. The advantage of the weight-change measurement is that the effect of open porosity, which formed a network within many PDCs,[25] can easily be picked up. Such internal oxidation is important to characterize material degradation. However, it is difficult to use weight-change measurement to obtain the intrinsic parabolic rate constant without uncertainty. First, unlike crystal material, it is not easy to measure the composition of the amorphous material accurately; thus, the relationship between weight change and the thickness of the oxide layer is uncertain. In addition, polymer-derived ceramics always contain a small amount of residual that will be burned out at higher temperatures. The amount of residual, which depends on the processing conditions and varied from samples synthesized by different groups, strongly affects the oxidation weight change. Hence, the results from different groups cannot be compared. Such uncertainty can be removed by directly measuring the thickness of the oxide layer; thus, the data can be compared between different materials. Meanwhile, even though the internal oxidation cannot be revealed with thickness measurement, the relatively accurate rate constant obtained by the thickness measurement can be used to obtain a better understanding of the weight-change data.
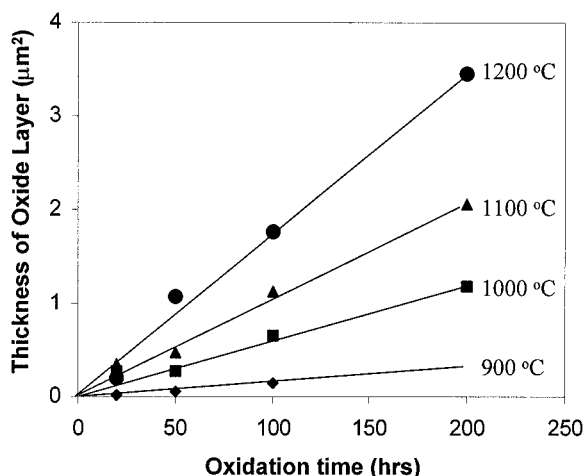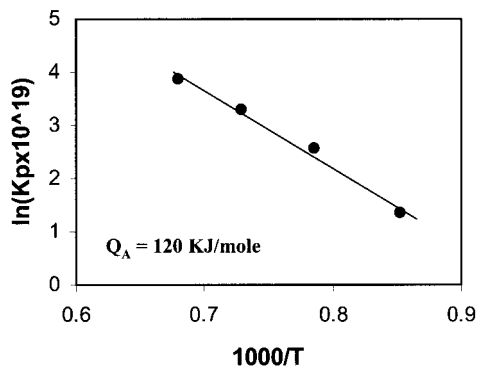

Fig. 4. Square of the thickness of the oxide layer, at different temperatures, plotted against time. The linear relationships indicated the oxidation follows a typical parabolic kinetics.

Fig. 5. Plot of log oxide layer thickness as a function of reciprocal of temperature. A relatively good linear relationship is obtained. The activation energy was calculated to be 120 kJ/mol.

IV. Summary

In summary, the oxidation behavior of a polymer-derived amorphous silicon carbonitride (SiCN) ceramic has been studied. In this paper, the oxidation kinetics was investigated by measuring the thickness of the oxide scale growing on the surface of fully dense disks. Our results clearly demonstrate that the growth of the oxide layer follows parabolic kinetics in the temperature range 900°–1200°C. The measured activation energy is close to that for SiC, which suggests that, at the testing temperatures, the oxidation of the SiCN is similar to that of SiC, albeit different from Si_3N_4, even though the SiCN contains a relatively high amount of nitrogen.

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