Controlled Atmosphere Pyrolysis of Polyureasilazane for Tailored Volume Fraction Si₃N₄/SiC Nanocomposites Powders

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Abstract

A controlled atmosphere pyrolysis process is used to develop processing protocols for controlled volume fraction $\text{Si}_3\text{N}_4/\text{SiC}$ composites from a polyureasilazane. Various processing protocols are explored such as gas composition (Argon, NH_3 and a 10% NH_3 /Argon mix) and a gas switching process where gas is switched from NH_3 to Argon at specified temperatures and specified times to quench the reaction. Results showed an accurate control of the volume fraction of SiC in 0 – 30 volume % range in a Si_3N_4 matrix. FTIR spectroscopic results confirmed that a substitution reaction occurs between NH_3 and the polyureasilazane. Raman spectroscopy shows a free carbon phase present up until 1850 °C and carbon present in specimens that do not show observable XRD peaks of SiC.

Keywords

Polymer-derived ceramics; Silicon nitride; Silicon carbide; nano-composites; crystallization

1. Introduction

Silicon nitride is an excellent structural ceramic that exhibits high mechanical strength and fracture toughness.[1] However, its high temperature use is hindered because its intergranular glassy phase softens at high temperatures causing grain boundary sliding leading to poor creep and strength properties.[2] It was discovered by Niihara et al. that the addition of SiC nanoparticulate reinforcing phase greatly improves these high temperature properties leading to the “Nanocomposite Concept”.[3] As such, numerous ways have been explored to incorporate SiC nanoparticulates into the Si_3N_4 matrix including: addition of SiC nanopowders[4], *in-situ* carbothermal of carbon and SiO_2 additives[5], and preparation of amorphous-SiCN powders followed by crystallization.[3,6,7]

The addition of SiC nanoparticles to Si_3N_4 powders through traditional powder processing routes leads to SiC agglomerates.[4] The ability to produce amorphous SiCN allows for fine dispersions of SiC, as the SiCN powders will nucleate and grow Si_3N_4 and SiC during the sintering/crystallization process. It is possible to develop SiCN powders through CVD[3,8], combustion synthesis[9] or plasma synthesis.[6] However, these methods are expensive, time consuming and require specialized equipment. This research uses the polymer-derived ceramic (PDC) processing route as it allows the possibility to finely tune the SiCN composition in the production of $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposites[7,10-12].

Polysilazane polymers (such as the commercially available Ceraset® Polyureasilazane (KiON Defense Technologies, INC, Huntingdon Valley, PA, USA)), are precursors to amorphous SiCN when pyrolyzed at temperatures of 800 – 1500 °C. The chemistry of the starting precursor will dictate the final composition of the SiCN ceramic and thus the resulting ratio of crystalline phases as dictated in the ternary diagram in Fig.1. If a precursor results in a

composition within the SiC-N-Si₃N₄ triangle, it will result in a metastable Si_{x+3}C_{x+y}N₄ phase.

When heated to temperatures >1500 °C the material will crystallize into Si₃N₄ and SiC with free carbon left in the system followed by carbothermal **reaction** (Eq. 1).[13,14] The composition will then follow the dashed line in Fig. 1 until all of the free carbon has reacted, resulting in a Si_{3+x}C_xN₄ composition with only stoichiometric Si₃N₄ and SiC remaining. It is ideal to produce SiCN powders within the shaded region of Fig. 1 to minimize the production of nitrogen gas during carbothermal **reaction**.

Fig. 1 also represents how one can control the Si₃N₄:SiC ratio by controlling the composition of SiCN. This can be advantageous for producing Si₃N₄/SiC nanocomposites since it will lead to nanoscale SiC of controlled volume fraction in a Si₃N₄ matrix leading to tailored properties.[15,16]

One way to control the PDC composition is by selecting different polysilazanes. However, only a few companies in the world produce this type of precursor and the available chemistries are limited. An alternative approach to controlling the chemistry of a SiCN PDC is by pyrolyzing the polymer in a reactive atmosphere. It is well known when polysilazanes are pyrolyzed in a NH₃ atmosphere they produce Si₃N₄ with no SiC.[17-19] By controlling the reaction process between the polymer and the NH₃ atmosphere, it is possible to precisely tailor the resultant SiCN composition. Previous studies have taken advantage of this reaction by utilizing various gas mixtures and heat treatment schedules to produce bulk SiCN PDCs with

controlled C:N ratio.[19] This study presents a novel process to produce SiCN powders with controlled C:N ratio that can be used for producing Si₃N₄/SiC nanocomposites.

Figure 1. Schematic illustrating the thermodynamic decomposition process of a SiCN PDC during heat treatment (this Figure is a modified version of the one presented in Ref. 19).

2. Experimental Procedure

Commercially available KDT Ceraset® Polyureasilazane (KiON Defense Technologies, INC, Huntingdon Valley, PA, USA) was used for all experiments. The precursor is a low viscosity liquid that is very sensitive to oxygen and moisture. Therefore, the precursor was handled within a dry nitrogen glove box and all heat-treatments were conducted under flowing gettered-Argon and high purity NH₃ or 10%NH₃/Ar gas mixes (Praxair, Inc. USA).

2.1 Cross-linking

A 30 mL batch of Ceraset was cross-linked in a horizontal quartz tube furnace under flowing gettered-Argon (flow rate of 0.1 l/min) at a heating rate of 10 °C/min to 400 °C for 1 hour. The cross-linked Ceraset was then cooled to room temperature under the flowing gettered-Argon and transferred to the nitrogen glove box. After cross-linking, the Ceraset becomes a brittle solid polymer, which can be crushed to a fine powder. The cross-linked Ceraset was broken into small pieces using a mortar and pestle and sealed in a methacrylate vial with 5 mm zirconia balls at a 4:1 ball:charge weight ratio. The powder was then milled in a high-energy ball mill (SPEX 8000M Mixer/Mill, SPEX SamplePrep, LLC, Metuchen, NJ, USA) for 100 minutes. The powder was then sieved with a 125 µm sieve. Particle size analysis was conducted on three random batches of powders (Horiba LA-960 Laser Particle Size Analyzer, Horiba Instruments Inc., Clifton Park, NY, USA) with iso-propyl alcohol as a liquid medium to check the reproducibility of the particle size and size distribution. Thermal gravimetric analysis (TGA) was carried out in flowing Argon at 2 °C/min to 1400 °C to determine optimal pyrolysis temperature (Netzsch STA409C, Netzsch Thermal Analysis, Selb, Germany).

2.2 Pyrolysis and Crystallization

Five grams of cross-linked powder was used for each pyrolysis run and placed in a 2" x 4" silica crucible. Heat-treatment was conducted in a horizontal quartz tube furnace with a 4" length uniform hot zone. Pyrolysis was conducted under a variety of conditions specified in Figure 2 and Table 1. Table 1 also includes the volume fraction of the different crystalline phases (details presented in Section 3). For Pyrolysis I experiments, the cross-linked powder was heat treated at 2 °C/min to 1050 °C for 2 hours under flowing gettered-Argon, NH₃ or a

10%NH₃/Argon mix at a flow rate of 0.1 l/min. For Pyrolysis II & III experiments, the cross-linked powders were heat treated in a flowing (0.1 l/min) reactive ammonia atmosphere (NH₃ or 10%NH₃/Argon) at 10 °C/min to 400 °C then at 2 °C/min to a specified temperature (T_s) and held at that temperature for a specified time (t_s) at which point the flowing gas was switched to gettered-Argon at a flow rate of 10 l/min for 5 minutes to allow the tube to be purged of the reactive gas. After 5 minutes of purging, the flow rate was lowered to 0.1 l/min and the furnace was heated at a rate of 2°C/min to 1050 °C for 2 hours as shown in Figure 3. Table 1 presents all test conditions used. After pyrolysis, the powders were milled in a high energy ball mill for 100 minutes using a Si₃N₄ vial with 1 mm Si₃N₃ balls at a 2:1 ball:charge ratio in a hexane milling medium. The milled slurry was then dried at 70 °C for 5 hours and the resultant powder was sieved through a 125 µm mesh. The powder was then uniaxially pressed with a 0.5” steel die at 100 MPa. The pressed pellets were then heat-treated in a resistive heated graphite furnace at 10 °C/min to 1650 °C for 2 hours under N₂ atmosphere (Centorr E10-2421, Centorr Vacuum Industries, Nashua, NH, USA). Most of the results presented in this paper are for samples crystallized at 1650 °C. Additional pyrolyzed pressed pellets from the 10NH₃550C series of heat treatments were crystalized at 1750 and 1850 °C for Raman analysis.

Figure 2. Flow diagram showing processing procedures and pyrolysis schedules in various atmospheres.

Table 1. Heat-treatment schedules with represented gas, switching temperature and switching time and resulting volume % β -SiC, α -Si₃N₄ and β -Si₃N₄.

Sample ID	Gas	Switching Temperature T _s (°C)	Switching Time t _s (min)	Vol%		
				β -SiC	α -Si ₃ N ₄	β -Si ₃ N ₄
N ₂ 1050	Ar	N/A	N/A	75.2	24.8	0
10NH ₃ 1050	10%NH ₃ /Ar	N/A	N/A	8.6	66.6	24.8
NH ₃ 1050	NH ₃	N/A	N/A	0	97.4	2.6
NH ₃ 560	NH ₃	560	0	32.4	57.3	10.3
NH ₃ 580	NH ₃	580	0	13.8	75.6	10.6
NH ₃ 600	NH ₃	600	0	0	89.5	10.5
NH ₃ 620	NH ₃	620	0	0	88.9	11.1
NH ₃ 570_10m	NH ₃	570	10	21.2	68.9	9.9
NH ₃ 570_60m	NH ₃	570	60	0	98.0	2.0
10NH ₃ 570_60m	10%NH ₃ /Ar	570	60	20.9	72.6	6.5
10NH ₃ 570_300m	10%NH ₃ /Ar	570	300	4.0	94.3	1.8
10NH ₃ 550_60m	10%NH ₃ /Ar	550	60	33.9	53.0	13.1
10NH ₃ 550_80m	10%NH ₃ /Ar	550	80	19.6	67.6	12.8
10NH ₃ 550_90m	10%NH ₃ /Ar	550	90	15.8	71.3	12.9
10NH ₃ 550_120m	10%NH ₃ /Ar	550	120	11.5	76.7	11.8
10NH ₃ 550_180m	10%NH ₃ /Ar	550	180	2.3	84.4	13.3
10NH ₃ 550_300m	10%NH ₃ /Ar	550	300	0	87.3	12.7

Figure 3. Heat-treatment schedule for controlled NH_3 pyrolysis where the flowing gas switches from NH_3 to Argon at a specified temperature (T_s) and a specified time (t_s).

2.3 Characterization

The crystallized pellets were ground in an agate mortar and pestle for X-Ray Diffraction (XRD) (Bruker D8 FOCUS, Bruker AXS Inc., Madison, WI, USA) analysis to identify and quantify the phases present in the crystallized PDCs. A Cu-K α source with a 40kV accelerating voltage and 40mA and a scanning range of 20 to 65 $^{\circ}2\theta$ at a step size of 0.02 $^{\circ}2\theta$ was carried out on all samples. A curved graphite monochromator (Cu-Monochromator, Bruker AXS Inc. Madison, WI, USA) with a diffraction angle of 26.4 2θ was used to increase the resolution of the diffraction pattern for phase quantification. Phase quantification was determined by the multiline “Mean-Normalized-Intensity” (MNI) technique, which involves selecting a few unresolved peaks and then calculating the angle and structure contributions to the integrated peak intensities. The only unknown factor is the volume fraction of the component phase.[20,21] In

this procedure, the integrated intensity of a Bragg peak j of phase i in a Bragg-Brentano diffraction pattern can be expressed as

$$I_{ij} = \frac{K(mL_p|F|^2)_{ij}(v_i/V_i^2)}{2m} \quad (2)$$

where K is an instrument constant, m is the multiplicity factor, L_p the Lorentz-Polarization factor, $|F|$ the structure amplitude, v_i the volume fraction of phase i , V_i the unit cell volume of phase i , and μ the linear attenuation coefficient of mixture. These integrated intensities are converted to normalized intensities (I_{ij}^n) according to

$$I_{ij}^n = \frac{I_{ij}}{R_{ij}} \quad (3)$$

where

$$R_{ij} = \frac{(mL_p|F|^2)_{ij}}{V_{ij}^2} \quad (4)$$

is the normalizing factor for peak j of phase i . The volume fractions of each phase can then be calculated by

$$v_i = \frac{\bar{I}_i^n}{\sum_p \bar{I}_p^n} \quad (5)$$

where summations are take over all p phases of the sample. Normalizing factors for α,β -Si₃N₄ and β -SiC were used from reference [21].

FTIR (Vertex 70, Bruker AXS Inc., Madison, WI, USA) measurements were performed on Ceraset crosslinked at 400 °C and milled into a fine powder. Measurements were also taken on crosslinked powders heat treated in 10%NH₃/Ar atmosphere at 550 °C for 0, 60, 120, 180 and 300 minutes and crosslinked powders heat treated in gettered-Argon at 550 °C for 60 and 300 minutes. These samples were cooled immediately after the 550 °C heat treatment in order to

remain in their transient state. The powder samples were mixed with KBr (1:100 sample:KBr weight ratio) and pressed into a transparent pellet. Samples were scanned in transmission mode from $4000 - 400 \text{ cm}^{-1}$ at a step size of 4 cm^{-1} .

Pyrolyzed pressed powder pellets (1050°C) as well as pellets crystallized at 1650, 1750 and 1850°C in a nitrogen atmosphere were hand polished with 1600 grit SiC paper for Raman Spectroscopy sample preparation. Raman Spectroscopy (Renishaw inVia Raman Microscopy, Renishaw Inc., Hoffman Estates, IL, USA) using a 785 nm laser excitation source was used to cover a scan range of $2000 - 500 \text{ cm}^{-1}$.

3. Results and Discussion

Galusek *et al.* [3] observed a carbon gradient when attempting to produce bulk SiCN ceramics from poly(hydridomethyl)silazane treated with NH_3 gas. This suggests a solid-gas reaction at the interface between the flowing NH_3 gas and the crosslinked polymer. As such, there is possibility that variations in particle size could result in compositional differences. Therefore, it is pertinent to confirm uniformity of the particle size between batches of the crosslinked powders prior to pyrolysis under ammonia gas. Fig.4. shows that the particle size and size distribution of the crosslinked powders is consistent between each batch of the milled powders, with a D50 of $10.6 \mu\text{m}$.

Figure 4. Particle size analysis of 3 batches of crosslinked and milled Ceraset.

During pyrolysis under argon, the majority of decomposition is shown to be complete at ~800 °C, consistent with the literature[22], with a 13.7% weight loss as shown in Fig.5. Therefore, 1050 °C was chosen as a final pyrolysis temperature to ensure the organics are driven off and the resulting PDC is amorphous. There is a slight increase in mass in Fig. 5 above 750 °C, which is likely due to oxidation of the material since the TGA did not utilize gettered Argon but Argon from the high purity (99.9%). This observation stresses the importance of reducing oxygen partial pressure as low as practical. As a result, all cross-linking and gas phase reaction experiments used gettered Argon.

Figure 5. Thermogravimetric analysis of crosslinked Ceraset in argon.

3.1 Pyrolysis in NH_3 atmosphere

As stated previously, polysilazanes pyrolyzed under an ammonia atmosphere will produce Si_3N_4 . [17,18] Some studies have been done on the concentration of NH_3 affecting the resultant composition of the pyrolyzed PDC. These studies have shown that as long as NH_3 is present in the atmosphere during pyrolysis, than the final ceramic will contain little to no carbon. [19] Fig. 6 shows the XRD results of crosslinked Ceraset pyrolyzed under: Argon, 10% NH_3 /Argon and 100% NH_3 atmosphere, followed by crystallization at 1650°C. Ceraset pyrolyzed in an Argon atmosphere results in a very high volume fraction of SiC (75.2%). When pyrolyzed in a 100% NH_3 atmosphere, it results in Si_3N_4 with no observable SiC; however, Ceraset pyrolyzed in a 10% NH_3 /Argon atmosphere results in observable β -SiC (8.5 vol.%). These results are shown in Table 1. This is contrary to previous results that show little to no carbon when pyrolyzed in a

10%NH₃/Argon atmosphere. However, in previous studies a low carbon polysilazane (poly(hydridomethyl)silazane)[19] was used in comparison to Ceraset, which has a much higher carbon content. It should be pointed out that there is a difference in the α/β -Si₃N₄ ratio between the 10%NH₃/Argon and NH₃ atmospheres. The sample pyrolyzed under NH₃ atmosphere is nearly all α phase ($\alpha/\beta=37.5$), whereas there is a significant amount of β phase in the 10%NH₃/Argon sample ($\alpha/\beta=2.7$). It should also be pointed out that α -SiC was identified in the argon pyrolyzed sample (which was not taken into consideration for the volume % calculations).

Figure 6. XRD results of crosslinked Ceraset pyrolyzed (at 1050 °C for 2 hours) in Argon (bottom), 10%NH₃/Argon (middle) and NH₃ (top) atmospheres and crystallized at 1650 °C in N₂.

In Pyrolysis II experiments the effect of the temperature at which the gas was switched from ammonia to argon was investigated. This results in tailored vol. % SiC between 32 – 0 % SiC at T_S of 560 – 600 °C (Fig. 7). This indicates that the majority of the reaction takes place prior to 600 °C. This result confirms the observations from Mutin et al.[18] who showed, from TG-MS experiments in NH_3 of various types of polysilazanes, that the reactions are complete prior to 750 °C. Although it is possible to tailor the SiC content by pyrolyzing Ceraset in NH_3 at different temperatures, the temperature range to tailor the composite between 0 – 30 volume % SiC is very narrow ($\sim 40^\circ C$). This could make repeatability of this process very difficult, as a 5 °C change in T_S can have drastic affects on the resulting SiC.

Figure 7. Volume % SiC as a function of switching temperature (T_S) for Pyrolysis II experiments.

Pyrolysis III experiments focuses on reaction time as a variable to control the SiC content. The $NH_3/570C$ experiments tailored the SiC content from 21.2 – 0% at t_S from 10 – 60 minutes,

showing that time is an important variable to control the extent of the reaction (Fig 8). This time span (50 minutes) is a narrow window for accurately tailoring the SiC content so the gas was changed to 10%NH₃/Argon for the 10NH₃570C experiments. The results showed tailored SiC content from 21 – 4% SiC at t_s from 60 – 300 minutes, which is a wide time frame to accurately tailor the SiC content. However, this study's goal was to tailor the SiC between 0 – 30 volume % as this is the common range to study SiC as the reinforcing phase of nanocomposites. The temperature was then reduced to 550 °C for the 10NH₃550C experiments. The SiC content was accurately tailored from 33.9 – 0% at t_s from 60 – 300 minutes as shown in Fig. 8.

Figure 8. Volume % SiC as a function of switching time (t_s) for Pyrolysis III experiments.

3.2 Spectral Characterization

In order to have a better understanding of the reactions that are occurring, FTIR experiments of the 10NH₃550C series were investigated and compared to the FTIR spectrum of the crosslinked powder (Fig. 9). After treating the crosslinked powder in the 10% NH₃ atmosphere at 550 °C there is a noticeable decrease in the Si-H absorption band (2129 cm⁻¹), which continues to decrease with time until it completely disappears at 120 minutes. There is also a decrease in the Si-CH₃ characteristic band (1255 cm⁻¹) along with decreases in C-H vibrations (2957 and 2900 cm⁻¹) and C-H deformation modes (1403 cm⁻¹) with increasing reaction time. This decrease in intensity bands is also accompanied by both an increase in intensity and broadening of the N-H absorption band (3340 cm⁻¹). These results confirm the hypothesis that this is a substitution reaction where -H and -CH₃ groups are substituted with -NH₂ represented by Eq. (6). [18,19] Mutin et al. [18] stated that it is likely that the substitution reaction with Si-H bonds predominates the reaction over Si-CH₃, which is supported by the results in Fig. 9 since the Si-H band disappears after 60 minutes, whereas, Si-CH₃ and C-H peaks disappear over a longer period of time.

Figure 9. FTIR spectrum of Ceraset crosslinked at 400 °C (Ar400C) and heat-treated in 10%NH₃/Argon atmosphere at 550 °C for 0 min. (10NH₃550C 0m), 60 min. (10NH₃550C 60m), 120 min. (10NH₃550C 120m), 180 min. (10NH₃550C 180m), and 300 min. (10NH₃550C 300m).

The results in Fig. 9 corroborate the hypothesis that this reaction is a substitution reaction. However, Riedel et al.[22] showed a decrease in intensity of Si-H, Si-CH₃, and C-H with an increasing temperature under Argon atmosphere of Ceraset. To ensure the results in Fig. 9 are from the substitution reaction and not from thermal decomposition, a comparison study was conducted between crosslinked powders heated in the 10% NH₃ atmosphere vs. an Argon atmosphere (Fig. 10). Fig. 10 shows that crosslinked Ceraset heated in Argon at 550 °C for 60 minutes compared to the 10% NH₃/Argon treated sample. The Argon treated sample still retains the Si-H bond, whereas the 10NH₃/Ar sample has no observable Si-H band, thus supporting the

substitution reaction (Eq. (6)). There is also a significantly larger and broader N-H band present in the 10%NH₃/Argon sample compared to the Argon treated sample.

Figure 10. FTIR comparison of crosslinked Ceraset heat-treated at 550 °C in either Argon or 10%NH₃/Ar for 60 min.

Raman Spectroscopy is an excellent method to confirm the presence of carbon, and the type of structure that is formed.[23,24] Fig. 11 shows the Raman spectroscopic data for the 10NH₃550C_60 min (Fig. 11a) and 300 min (Fig. 11b) at temperatures ranging from 1050 to 1850 °C. The 1050 °C spectra shows no discernable peaks except two broad peaks between 1200-1700 cm⁻¹ for 10NH₃550C_60 min sample. At 1650 °C there are two large distinct peaks at 1302 and 1598 cm⁻¹ labeled D and G band respectively. These two peaks are common Raman

bands for disordered graphitic-like carbon. The higher energy G band is caused by vibrational modes of graphitic layers and the lower energy D band is caused by glassy carbon and nanocrystalline graphitic carbon. Because these bands are not sharp distinct peaks for the 1050 °C spectra, it is likely the carbon is completely amorphous at this stage.[23-25] The D and G bands still remain in the spectra until 1850 °C when they disappear, likely due to the last of the carbon being consumed from the carbothermal reaction with the Si_3N_4 (Eq. 1). It is an unusual result as these Raman bands usually disappear by 1600 °C in polymer-derived polysilazane ceramics.[25] Riedel et al. showed that Ceraset pyrolyzed in Argon had observable carbon up to 1600 °C but the bands disappeared at 1700 °C, whereas the bands do not disappear until 1850 °C for the 10NH₃550C treated samples. The 10NH₃550C_300 min sample showed D and G bands up to 1850 °C indicating that free carbon exists in this sample even though XRD data did not show observable SiC. It is likely that the carbon content is so low that the small volume fraction SiC is not observable in the XRD. Also, the 10NH₃550C_300 min sample did not show any Raman bands associated with SiC, which should occur at 798 and 802 cm⁻¹ as it does in the 10NH₃550C_60 min sample. Previous results have shown via elemental analysis that small amounts of carbon will still exist in NH₃ treated polysilazanes, which supports the results seen in Fig. 11b.[17-19]

Figure 11. Raman spectra of pyrolyzed Ceraset treated in a 10%NH₃/Argon atmosphere at 550 °C for (a) 60 min. and (b) 300 min and heat-treated to 1650, 1750 and 1850 °C.

4. Conclusion

This work showed that a novel controlled NH₃ pyrolysis process can be used to tailor the C:N content of SiCN powders for Si₃N₄/SiC nanocomposites. The results show that gas concentration, maximum reaction temperature (T_S) and reaction dwell time (t_S) all affect the stoichiometry of the SiCN PDC. FTIR results confirmed previous hypotheses that the reaction **between the NH₃ molecules and polysilazane** occurs due to a substitution reaction where **–H and –CH₃ groups are substituted by –NH₂**. Raman spectroscopy results showed that free carbon exists in the powders up until 1850 °C. It also showed carbon existing in samples that did not have observable XRD peaks of SiC. It is possible to use this novel process for any type of polysilazane polymer to produce SiCN powders for Si₃N₄/SiC nanocomposites with varying SiC content.

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