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Thermal stability of polymer derived SiBNC ceramics

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Abstract

To study the thermal stability of polymer derived SiBNC ceramics, a polyborosilazane was pyrolyzed in N_2 and NH_3/N_2 atmosphere, respectively. The as-pyrolyzed products were annealed in N_2 atmosphere at 1200–1850 °C for 2 h. The chemical composition and phase structure of the as-pyrolyzed and annealed ceramics were investigated by element analysis, XRD and FT-IR. The results show that all the ceramics exhibit excellent high temperature stability. They are fully amorphous to 1700 °C, and only partial crystallization, giving a mixture of Si_3N_4, BN and SiC phases, is observed upon heating at 1850 °C. The N_2 pyrolyzed products show better stability than the NH_3/N_2 pyrolyzed products and have less tendency to crystalline at higher temperatures. Better retention of nitrogen at high temperatures is also observed for the N_2 pyrolyzed products.

Keywords: A. Calcination; B. X-ray methods; C. Thermal properties; Si–B–N–C ceramics

1. Introduction

The synthesis of multinary systems composed of silicon, boron, nitrogen and carbon via pyrolysis of element-organic polymers is an interesting field in high performance materials in recent years [1–16]. One of the most striking features of polymer derived SiBNC ceramics over binary or ternary compositions is their remarkably high resistance toward thermally induced degradation or decomposition even at very high temperatures [1,2,5,7,17–19]. The thermal stability of the polymer derived amorphous ceramic materials includes (1) chemical stability that is related to the decomposition of the materials and (2) structure stability which is associated with crystallization and phase transition process.

As is known, the composition of a material has important influence on its properties and the polymer derived SiBNC ceramics are not exceptional. Although the influence of Si/B/N/C ratio on the materials' high temperature properties is still not known in detail, each element has its respective effect on the high temperature properties of this ceramic material. For example, boron plays a major role in stabilizing the metastable amorphous phase and suppressing the thermal degradation of the ceramic matrix [1,5,17]. However, its influence on the high temperature properties varies with the boron content of the ceramics. Comparison of the composition of different SiBNC ceramics points to the fact that materials with a low (<3 wt%) or a high (16–18 wt%) boron content are less well protected from thermal degradation [5,17]. As to the nitrogen content, from the thermal stability point of view, it should not be too high, since substantial amounts of silicon nitride negatively influence the high temperature stability of the SiBNC ceramics [20]. The presence of carbon influences the electrical properties and the high temperature stability of the SiBNC ceramics. Decreasing the carbon content always results in a decreased dc-conductivity. Carbon in the form of SiC always has positive influence on the thermal stability of the ceramics. The free carbon tends to crystallize to form graphite phases which greatly impair the mechanical properties of the material [12,13,20–24].

The diversity of the composition and structure of the polymer derived SiBNC ceramics might not only be caused by precursor composition and structure but also be due to the pyrolysis conditions, i.e. the pyrolysis atmosphere and temperature. In spite of the great importance of such class of novel materials, relatively few works have reported on the SiBNC ceramics obtained from the same polyborosilazane pyrolyzed in different atmospheres, with investigations of the chemical and structural stabilities of this novel multinary ceramic. Accordingly, an understanding of the amorphous–crystalline transformation is very important for developing

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methods to retain the amorphous state in the SiBNC ceramics [25].

To better understand the effect of pyrolysis atmosphere on the thermal stability of the polymer derived SiBNC ceramics, in this paper, we firstly obtained two SiBNC ceramics with different composition and structure through pyrolysis the same polyborosilazane under N_2 and NH_3/N_2 atmosphere, respectively; secondly, to compare the thermal stability of the two SiBNC ceramics derived from the same polymer but with different composition and structure, the two ceramics were annealed in inert atmosphere at temperatures between 1000 and 1850 °C; and then the compositional and structural variations of the two SiBNC ceramics bulk samples during the whole heat treatment were investigated.

2. Experimental procedure

The synthesis of the polyborosilazane used in present study is described in a previous paper published separately [26]. Pyrolysis of bulk preceramic material was performed in Al_2O_3 Schlenk tubes in a flowing N_2 or NH_3/N_2 atmosphere (25–1000 °C, heating rate, 5 °C/min followed by a dwell time of 2 h at 1000 °C). The crystallization of the as-obtained amorphous ceramics was performed in graphite furnaces using graphite crucibles (heating rates, $T < 1400$ °C, 10 °C/min; $T > 1400$ °C, 2 °C/min; dwell time, 2 h) in N_2 atmosphere.

Chemical analysis was performed using a combination of different analysis equipment (C/S Determinator, Model CS-444, LECO, Joseph, MI; N/O Determinator, Model TC-436, LECO, Joseph, MI) and by atom emission spectrometry (ICP Spectrometer, Model JY70 Plus, ISA JOBIN YVON, Longjumeau, France). The molecular structures of the polymer and ceramic samples were interpreted by using Fourier transform infrared spectroscopy (FT-IR; Model Avatar 360, Thermo Nicolet, Madison, WI). The phase structures of the ceramic samples were characterized by X-ray diffraction unit (XRD, Model D8 ADVANCE, Bruker AXS, Karlsruhe, Germany,) analysis at room temperature, with Cu Kα radiation and nickel filter. The samples were powdered in a WC ball mill prior to analysis.

3. Results and discussion

3.1. Composition of SiBNC ceramics

The composition of the polymer derived ceramics is determined by precursor chemistry and is affected by pyrolysis conditions. The compositions of the ceramics pyrolyzed in N_2 and NH_3/N_2 are plotted as a function of temperature in Fig. 1, respectively. The decomposition behaviors of the ceramics obtained in both atmospheres are very similar. A comparison of the as-synthesized polymer with the ceramics annealed at different temperatures revealed that the carbon contents are significantly reduced when the polymer was pyrolyzed at 1000 °C. The carbon contents remain almost constant when the ceramics were annealed at higher temperatures. Obviously, the NH_3 pyrolyzed ceramics have a significantly lower carbon content (~0.5 wt%) than the N_2 pyrolyzed ceramics (~10 wt%), which is also reflected in the sample color that former are black while the latter are white. The facile loss of methane has been observed in the ceramic conversion of a variety of silicon preceramic polymers that contain saturated methyl groups [25] and the efficiency of this process can account for the low carbon content of the polymer derived SiBNC ceramics.

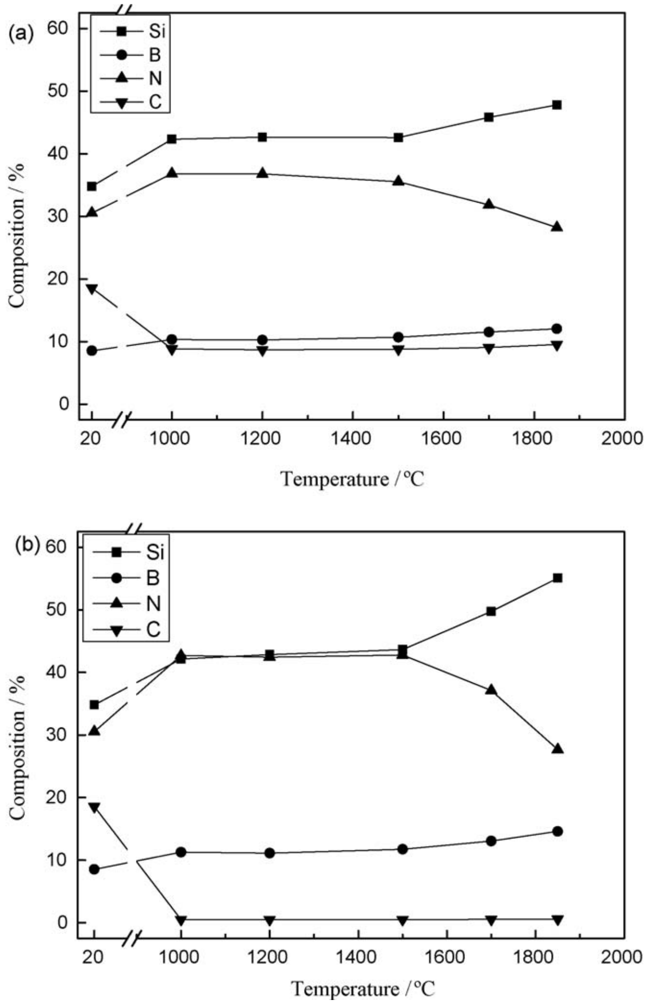

Fig. 1. Dependence of composition on annealing temperature in SiBNC ceramics pyrolyzed in N_2 (a) and in NH_3/N_2 (b).

The decrease of carbon content result in the increase of the relative contents of Si, B and N after the polymer was pyrolyzed. During the annealing process, the nitrogen content of the ceramics decreased when the temperature was raised to 1500 °C while the silicon content remain increasing before the temperature was raised to 1700 °C. The boron content of the ceramics increased during the whole annealing process. As the major difference, the carbon content of the NH_3/N_2 pyrolyzed ceramics (<0.5 wt%) is lower than the N_2 pyrolyzed products (10 wt%), however, the NH_3 pyrolyzed ceramics have larger nitrogen content than the N_2 pyrolyzed products.

The carbon reduction for both cases mainly involves the loss of methyl groups which partly evolve as methane during the

$$[\equiv N-H]+[H_3C-Si\equiv]\rightarrow[\equiv N-Si\equiv]+CH_4$$

Scheme 1.

$$3\equiv Si-CH_3+NH_3\rightarrow N[Si\equiv]_3+3CH_4$$

Scheme 2.

$$Si_3N_4+3C\longrightarrow 3SiC+2N_2$$

Scheme 3.

$$Si_3N_4\longrightarrow 3Si+2N_2$$

Scheme 4.

pyrolysis step though with different reaction mechanisms [27–29]. In N_2 atmosphere, the carbon reduction mainly involves the crosslinking reaction between different active groups in the polymer networks, as illustrated in Scheme 1.

In NH_3/N_2 atmosphere, the treatment reduces the carbon content by the formation of methane as described in Scheme 2. The substitution of carbon by nitrogen in the pyrolysis reaction in NH_3/N_2 atmosphere can account for the higher nitrogen content in the corresponding products. The lower carbon content SiBNC ceramics always have good dielectric behavior which can be of technological interest [23,24]. This enables to synthesize a variety of materials for electrical and electronic applications just by changing the composition and structure of SiBNC ceramics and the pyrolysis atmosphere is an efficient route.

When the temperature was raised to 1484 °C, the reaction of Si_3N_4 and carbon with formation of SiC and nitrogen, as illustrated in Scheme 3, lead to the decrease of nitrogen content of the ceramic materials [10]. However, the decreased value in the NH_3/N_2 pyrolyzed products is smaller than that of the N_2 pyrolyzed products, which may result from the lower reaction degree for the NH_3 pyrolyzed products because of the lower carbon concentration in the left hand of the reaction. The decomposition of the silicon nitride into silicon and nitrogen, as illustrated in Scheme 4, results in further decrease of nitrogen content when the temperature reaches 1840 °C [10].

Based on the analysis abovementioned, we can speculate that, the absolute content of B and Si should not change during the annealing process. Therefore, the B/Si ratio should remain constant in the whole temperature range investigated, which was verified in Fig. 2 showing the dependences of B/N and Si/B in the ceramics on temperature, respectively. The B/N ratio is about 0.4 and remains roughly constant up to 1500 °C. The B/N ratio increased due to the nitrogen vaporization, resulting from the reaction of Si_3N_4 and carbon at 1484 °C with formation of SiC and nitrogen gas (Scheme 3). Furthermore, the increased value of B/N in the N_2 pyrolyzed ceramics is larger than that of the NH_3/N_2 pyrolyzed products, that is, the former have a better retention of nitrogen at high temperature, exhibiting better thermal stability than the latter, which is consistent with the results reported in the literature [11]. The increased high temperature stability of carbon-rich compositions can be ascribed to the fact that carbon bonds to four neighbors via strong covalent bonds instead of three in the case of nitrogen [12,13].

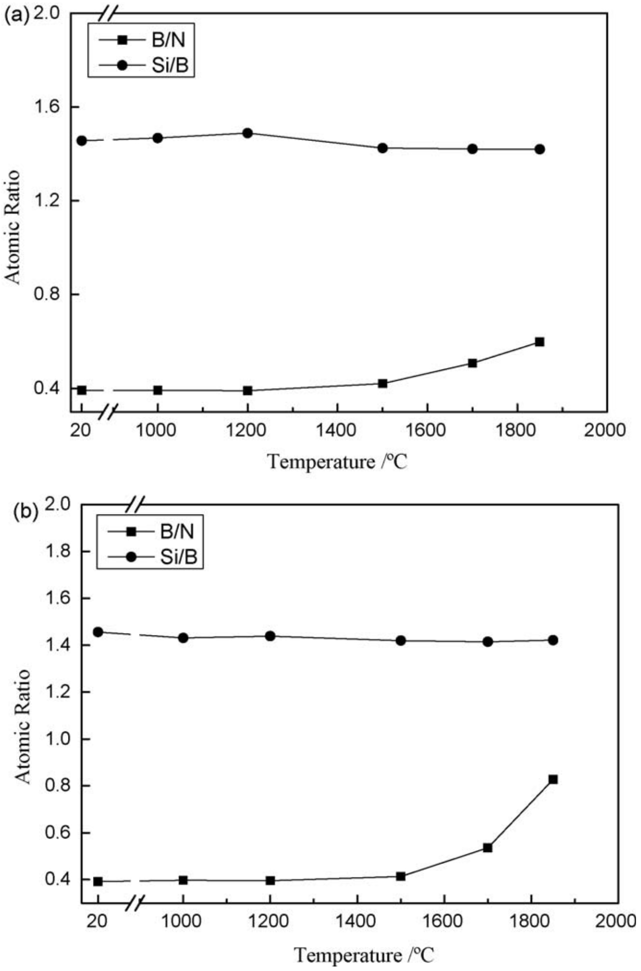

Fig. 2. Dependence of B/N and Si/B on annealing temperature in SiBNC ceramics pyrolyzed in N_2 (a) and in NH_3/N_2 (b).

To analyze the high temperature mass stability of the ceramic materials, char yields of polyborosilazane at different elevated temperatures up to 1850 °C in N_2 atmosphere were recorded. The results are shown in Fig. 3. Ceramic yields at 1000 °C in both atmospheres are very close, which is about 63 wt% and 61 wt% in N_2 and NH_3/N_2 atmosphere, respectively. As the temperature is raised, the NH_3/N_2 pyrolyzed ceramics have significant lower char yields than the N_2 pyrolyzed ceramics. The decreased value in char yield for the N_2 pyrolyzed and NH_3 pyrolyzed products at 1500–1850 °C is about 3.8 wt% and 10 wt%, respectively. Obviously, the N_2 pyrolyzed ceramics have better thermal stability than the NH_3 pyrolyzed ceramics.

3.2. Phase structure of SiBNC ceramics

One of the key issues when dealing with newly developed polymer derived ceramics is their stability at high temperatures, in particular, in the amorphous state. This is valid for the

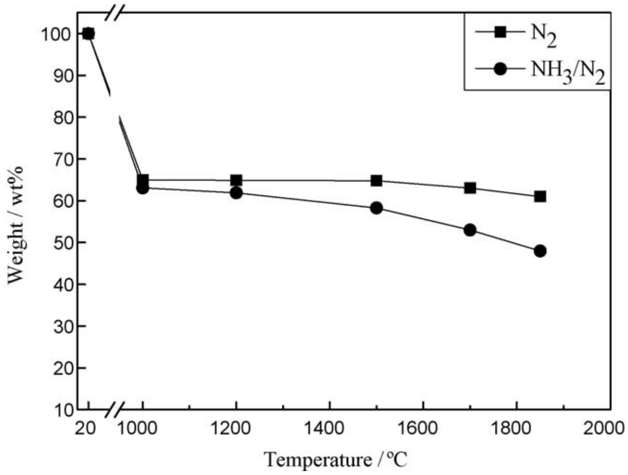

Fig. 3. Dependence of ceramic yield on temperature of polyborosilazane.

preparation of monoliths as well as for the preparation of coatings and ceramic fibers. Phase formation of the polymer derived SiBNC ceramics during the annealing treatment was studied by means of X-ray diffraction and infrared spectroscopy.

Typical XRD powder patterns are shown in Fig. 4 for various SiBNC samples. As expected and known from literatures [3,5–9,13,30], the as-pyrolyzed ceramics obtained either in NH_3/N_2 (Fig. 4a) or in N_2 (Fig. 4b) were amorphous by XRD as suggested by broad, featureless powder patterns. The amorphous state of the ceramic materials is maintained even after heating to 1700 °C in N_2 for 2 h. Significant crystallization did not occur in these samples until after heating in N_2 atmosphere to 1850 °C for 2 h, at which point a mixture of Si_3N_4, BN, and minor SiC phases was apparent. This result is consistent with the reported results [1–3,8,10,11] that polyborosilazanes remained primarily amorphous even after heating to 1700 °C in inert atmospheres. Samples that were pyrolyzed in NH_3/N_2 were more crystalline after heating at 1700 °C, and showed peaks indicative of poorly crystalline Si_3N_4 at $2\theta = 32°$. Increased heating to 1850 °C sharpened the XRD peaks, so that SiC, Si_3N_4, and BN phases could be distinguished. Obviously, the intensity of the crystalline in the NH_3/N_2 pyrolyzed ceramics is stronger than that of the N_2 pyrolyzed products, from which we may conclude that the NH_3/N_2 pyrolyzed samples have more tendency to crystallize than the N_2 pyrolyzed products when they are heated to higher temperatures. This result is in accordance with Schmidt et al.'s [11] observation that though the N_2 pyrolyzed products were more crystalline after annealing at 1600 °C, they have less crystalline than the NH_3/N_2 pyrolyzed products when heated to 1850 °C. The increased high temperature stability of carbon rich SiBNC ceramics was also reported by Jansen and co-workers [9,12,13]. They ascribe this result to the fact that carbon bonds to four neighbors via strong covalent bonds instead of three in the case of nitrogen.

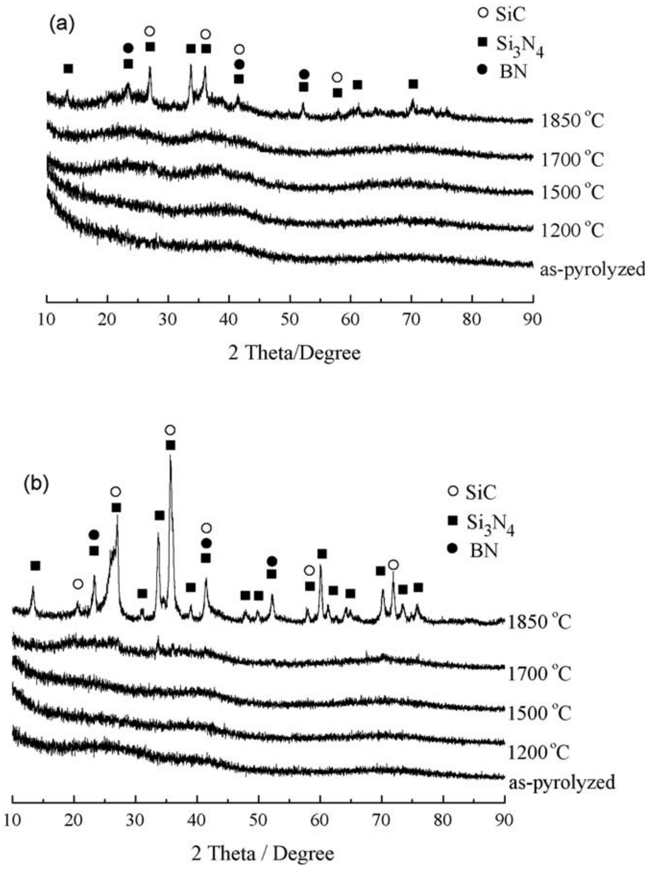

Fig. 4. XRD patterns of ceramics pyrolyzed in N_2 (a) and in NH_3/N_2 (b) annealed at different temperatures.

In Fig. 5 the IR spectra of the preceramic polymer, as-pyrolyzed materials, and annealed materials, which were obtained in transmission mode, are shown. The positions of the main absorption maxima of crystalline BN, Si_3N_4, and SiC are denoted. All spectra show a very broad absorption at about 1380 cm^{-1} characteristic for BN. The intensity of this band increases as the temperature increases for both ceramics, indicating the increase of BN phase content in the ceramics. In the ceramics which were annealed at 1700 °C and 1850 °C, the spectra show a very broad absorption at about 1380 cm^{-1} characteristic for crystalline h-BN. However, in the ceramics which were annealed below 1700 °C, the peak position for BN has a small shift toward higher wavenumbers which can be correlated to the amorphous state of BN phase. Such shifts were also found in the SiBNC ceramics reported by Muller et al. [10].

For the N_2 pyrolyzed products, the spectra of ceramics annealed below 1700 °C exhibit a broad band between 1100 and 500 cm^{-1} the maximum of which is located at about 900 cm^{-1}. This position approximately corresponds to that of the main absorption of crystalline Si_3N_4 (920 cm^{-1}) with a small bathochromic shift which can be expected in amorphous materials. For Si–C bonds, absorption maxima are centered at about 800 cm^{-1} in the ceramics which were treated below 1700 °C. Compared to crystalline SiC (850 cm^{-1}), the shift to lower frequencies can also be explained by the partly amorphous character of the materials [10].

In comparison, the IR spectra of the NH_3/N_2 and the N_2 pyrolyzed ceramics are very similar. The former show weaker intensity of SiC indicating the lower carbon content in the

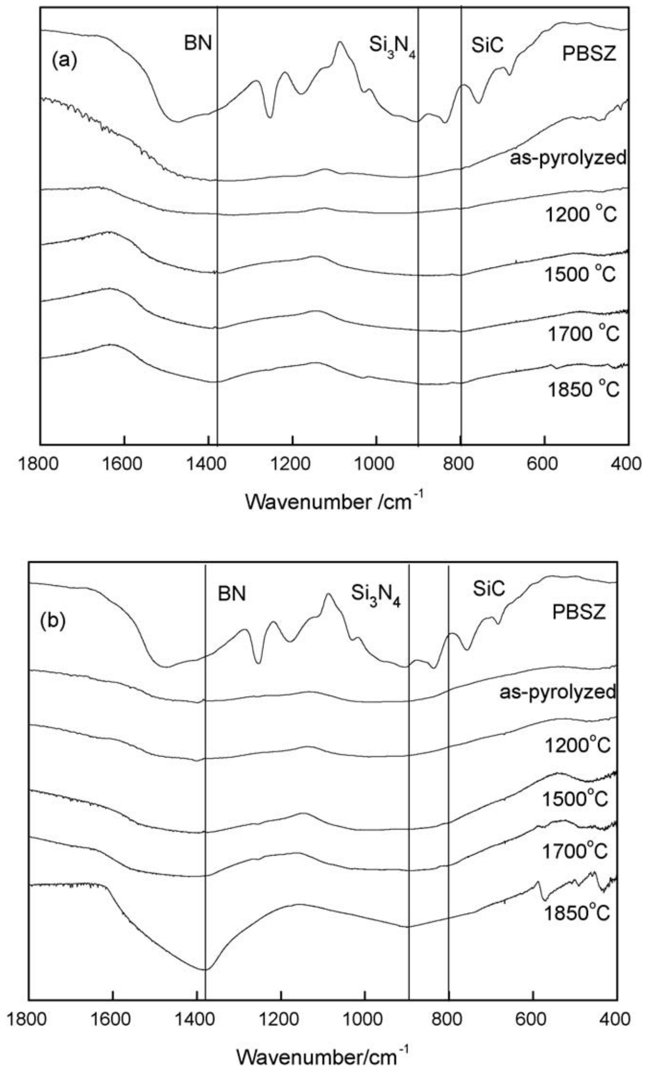

Fig. 5. IR spectra (1800–400 cm^{-1}) of PBSZ and products pyrolyzed in N_2 (a) and in NH_3/N_2 (b) annealed at different temperatures.

ceramics. Compared to the main absorption of ceramics obtained in N_2 atmosphere, the Si–X (X: C or N) vibration band in the NH_3/N_2 pyrolyzed ceramics is shifted to lower frequencies. This may indicate a larger relative amount of crystalline phases in these materials, which is in good accordance with the XRD results.

4. Conclusions

Thermal stability of SiBNC ceramics with different carbon content based on the compositional and structural variations at elevated temperatures were investigated. The ceramic products show excellent high temperature resistance, remaining fully amorphous up to 1700 °C in N_2 atmosphere and partial crystallines were found when heated at 1850 °C. The weight loss in N_2 atmosphere at 1500–1850 °C is about 3.8 wt% and 10 wt% for the N_2 and the NH_3/N_2 pyrolyzed products, respectively. The N_2 pyrolyzed products with high carbon content exhibit better amorphous structure stability than the NH_3 pyrolyzed products.

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