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Pyrolysis synthesis of Si–B–C–N ceramics and their thermal stability

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Abstract

Si–B–C–N ceramics were synthesized by co-pyrolyzing hybrid polymeric precursors of polycarbosilane (PCS) and polyborazine (PBN). The pyrolysis behavior and structural evolution of the hybrid precursor, the microstructure and composition of the prepared Si–B–C–N ceramics were fully investigated. It was found that the copyrolysis of hybrid polymeric precursors in Ar led to the release of CH_4, CH_3NH_2 and CH_3CN gases at temperatures ranging from 200 to 1100 °C, and finally resulted in the formation of amorphous Si–B–C–N ceramics. In particular, the Si–B–C–N ceramics formed from the hybrid precursor with PBN/PCS mass ratio of 1 could keep amorphous state up to the annealing temperature of 1800 °C with weight change of only 2.08%. But this amorphous ceramics would decompose to form crystalline SiC, BN and Si_3N_4 at 2000 °C. Additionally, compared with PCS-derived SiC ceramics, the Si–B–C–N ceramics showed improved anti-oxidation performance up to 1300 °C due to the formation of borosilicate layers covering the ceramics.

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

1. Introduction

Si–B–C–N ceramics with amorphous structure were reported to possess many excellent properties such as outstanding thermal stability against crystallization and decomposition [1,2], superior mechanical properties and better high-temperature anti-oxidation performance than pure SiC [3–5], which grant them potential applications in coatings [6,7], microelectronics [7], membranes [8] and high-temperature stable ceramic fibers for reinforcing composites [9,10]. Hence, more and more interest has been putting onto multiphase Si–B–C–N ceramics [1,11].

Many methods have been reported to prepare this kind of ceramics. Takamizawa et al. fabricated Si–B–C–N ceramics via a polymer-to-ceramic conversion route [12], which ensures the homogeneousness of the chemical compositions of the prepared ceramics in contrast with the conventional powder hot-press method [13]. Seyferth et al. explored thermolysis Si–B–C–N ceramics from silazane-substituted borazines by introducing silazanes into borane dimethyl sulfide [14,15]. Structurally comparable borazine-based Si–B–C–N polymers via thermal dehydrocoupling reaction of borazine with oligo- or polysilazanes were also reported [16–18]. Later, a route to the synthesis of borazine-based Si–B–C–N polymers by reacting B-chloroborazines with $LiSi[Si(CH_3)_3]_3$ followed by subsequent polymerization with hexamethyldisilazane was developed by Paine et al. [19], but the pre-ceramic polymers for Si–B–C–N ceramics were extremely pyrophoric and insoluble in most solvents [13]. However, among the polymer-derived Si–B–C–N ceramic preparation methods, polymers normally caused phase separation due to the intrinsically low entropy of mixing for linear molecules with large molecular weight [20], which made them difficult to be handled. In addition, polymeric precursors required intermediate steps, special setup and even special handling procedure for hazardous chemicals and the by-products of borane dimethyl sulfide, chlorosilanes, and ammonium chloride [21]. All these problems made preparation process difficult.

In this work, a simple and efficient route for preparing Si–B–C–N ceramics through co-pyrolysis of the soluble hybrid precursors of polycarbosilane (PCS) and polyborazine (PBN) polymers without additives or catalyst, was demonstrated. Amorphous Si–B–C–N ceramics with thermal stability up to 1800 °C could be fabricated. Investigating the structures and structural evolution of Si–B–C–N ceramics at high temperatures

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is essential to understand the relationship between structure and property that holds the key to the potential applications of the ceramics. Therefore, the thermal behavior of the hybrid precursors, the structures and thermal stability of the prepared Si–B–C–N ceramics were investigated in detail.

2. Experimental

PCS (main units: $[HSi(CH_3)CH_2]$, $[CH_2Si(CH_3)_2CH_2]$, $[Si(CH_3)_2Si(CH_3)_2]$) with a number-average molecular weight of about 1150 and a soften point of 210 ± 2 °C was purchased from National University of Defense Technology of China and used as the precursor of SiC. PBN ($[CH3(H)N]_3B_3N_3H_3$ and $[B(NHCH_3)_3]$) with a chemical formula $BN_{0.98}C_{0.99}H_{3.2}$, a number-average molecular weight of about 600 and a softening point of 61 ± 2 °C [22], was used as the precursor of BN. Analytical-grade xylene was employed as the dissolvent. The mixture precursors with PCS/PBN weight ratios of 2:1, 1:1 and 1:2 were labeled as P1, P2 and P3, separately. Table 1 shows the components of these mixture precursors. At first, the mixture precursors were dissolved into xylene at a mass concentration of 60% and mixed fully at room temperature under an inert atmosphere (Ar or N_2) to obtain a transparent solution with good fluidity. After removing xylene from the solutions in a rotary evaporator at 80 °C for 4 h and natural cooling to room temperature, white-yellow solid hybrid precursors were obtained. Then an alumina crucible loaded with the solid hybrid precursors was placed at the center of a tubular furnace. Prior to heating, the chamber was flushed with high-purity Ar to eliminate the residual air. The furnace was then heated to 1200 °C at a rate of 1 °C min^{-1} and held at this temperature for 2 h under Ar atmosphere. After cooled naturally to ambient temperature under the protection of Ar flow, the as-pyrolyzed Si–B–C–N ceramics were fabricated. To investigate the thermal stability, the Si–B–C–N ceramics prepared were loaded into graphite crucibles and annealed at 1450–2200 °C for 1 h at a heating rate of 2 °C min^{-1} under Ar atmosphere.

The pyrolysis behaviors of the precursors were investigated by thermogravimetry (TG, Netzsch STA 409), online Fourier transform infrared spectroscopy (FTIR, Tensor 27) combined with Mass spectrometry (MS, Balzers MID). The Si–B–C–N ceramics were characterized by X-ray diffraction data (XRD, PANalytical X'Pert PRO) with Cu Kα radiation ($\lambda = 0.15405$ nm), TG (Netzsch STA 409), FTIR (Tensor 27), scanning electron microscope (SEM, FEI Quanta 200) and transmission electron microscope (TEM, TECNAI G20) equipped with X-ray energy dispersive spectrometer (EDX).

3. Results and discussions

Fig. 1a and b shows the XRD patterns of the pyrolysis products from single PCS precursor and mixture precursors P1–P3 at 1200 °C and 1500 °C, respectively. It can be seen that all pyrolysis products at 1200 °C from the hybrid precursors are almost amorphous (Fig. 1a), whereas β-SiC (JCPDS no. 01073-1665) and carbon (JCPDS no. 01025-0284) phases appear in the pyrolysis product from single PCS precursor, which hint that the involvement of B and N into the precursors could restrain the grain growth of β-SiC phase from PCS. When the pyrolysis temperature increases to 1500 °C, β-SiC, *h*-BN (JCPDS no. 00035-1365) and carbon phases can be found in the pyrolysis products from P1 and P3, while the pyrolysis product from P2 is still in an amorphous state. For the pyrolysis product from single PCS at 1500 °C, α-SiC phase (JCPDS no. 00004-0757) is present in addition to β-SiC and C phases, indicating a phase transformation of SiC crystal [23]. Addition of B and N could obviously restrain the formation of SiC phase from PCS, and the grain size of SiC is related to the content of PBN precursor added. Appropriate amount of PBN is favorable for the formation of amorphous product (P2), while excess PBN is harmful to the formation of amorphous product (P1 and P3). It is speculated that the presence of B and N retards the diffusion of other atoms and hinders the formation of crystalline phases [24]. Moreover, the plus N existing in the hybrid precursor favors the generation of SiCN units that could restrain the crystallization until 1400 °C. Furthermore, SiCN could react with free carbon at more than 1450 °C in Ar and facilitate the crystallization of SiC [1,25].

Conversion process of the precursors was investigated by TG (Fig. 2). The mass loss of the mixture precursor can be divided into four distinctive stages: (i) an initial mass loss of 10% from room temperature to 300 °C due to the release of solvent and the oligomers; (ii) 6.3% mass loss between 300 and 500 °C, which is caused by the polycondensation of precursor; (iii) a large mass loss of 13.2% in the temperature range 500–800 °C, which can be ascribed to the decomposition of precursor, and (iv) a final mass loss of about 2.6% at 800–1100 °C, originating from the evolution of CH_4. The final product has a mass of about 67.9% relating to the original precursor. The PBN precursor shows a comparable ceramization progress marked by four decomposition steps. The largest mass loss in the temperature range 400–700 °C, which can be

Table 1
Chemical composition and empirical formula of the hybrid precursors with various PCS/PBN weight ratios.

Sample	Si	B	C	N	H	Si/B	Empirical formula
P1	34.6	9.08	36.63	11.47	8.22	3.81	$Si\,B_{0.68}C_{2.48}N_{0.66}H_{6.67}$
P2	25.95	13.62	34.95	17.21	8.27	1.91	$Si\,B_{1.36}C_{3.15}N_{1.33}H_{8.95}$
P3	17.3	18.17	33.26	22.94	8.33	0.95	$Si\,B_{2.73}C_{4.50}N_{2.66}H_{13.52}$

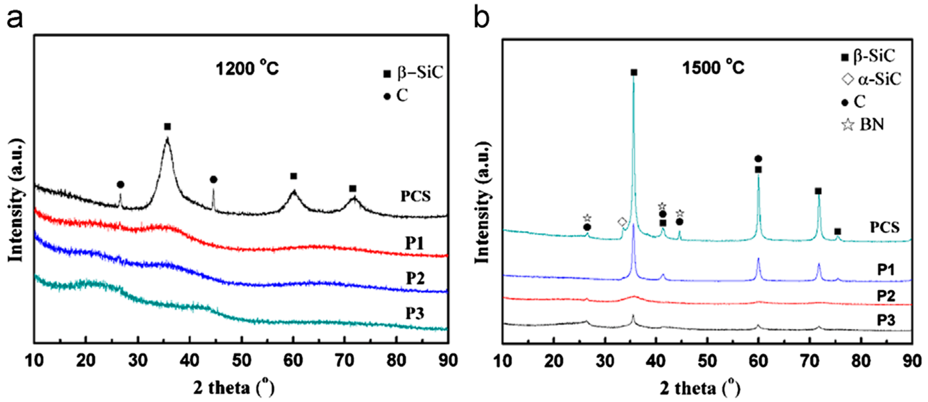

Fig. 1. XRD patterns of the samples pyrolyzed from PCS and hybrid precursors with various PBN/PCS weight ratios at (a) 1200 °C and (b) 1500 °C.

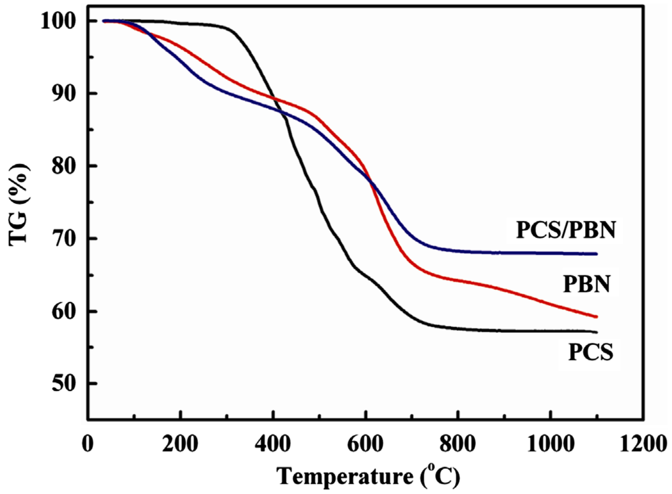

Fig. 2. TG curves of PCS, PBN and P2.

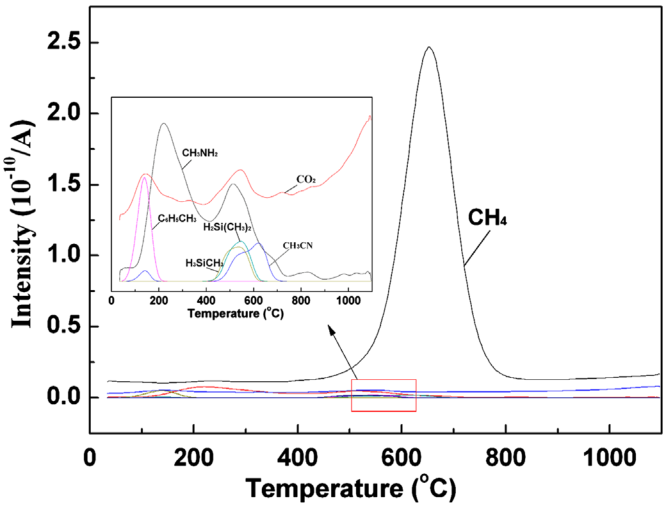

Fig. 3. MS spectra of the hybrid precursors of PCS and PBN.

attributed to the further condensation of methylamine and methane or its fragments from terminal methyl groups [26]. In contrast, PCS precursor shows a two-step decomposition behavior with the main weight loss in the temperature range 300–600 °C due to the polymerization of hydrosilylation and dehydrocoupling reactions accompanying the evaporation of low molecular weight molecules [27]. Additionally, mixture precursor results in a higher ceramic yield (67.9%) than single precursor of PCS (57.1%) and PBN (59.2%) because of the less mass loss in the early stage of decomposition, suggesting that the cross-linking between PCS and PBN could avoid violent evaporation of oligomers at high temperature during the co-pyrolysis process.

Fig. 3 shows mass spectra of the gases generated from thermal pyrolysis of hybrid precursor. The temperature dependence of intensity agrees well with the temperature dependence of TG curve of P2, and the maximum gas product occurs at 650 °C that is the same temperature for the appearance of the maximum loss during pyrolysis process. The release of CO_2, methylbenzene, CH_3NH_2, and CH_3CN from room temperature to 300 °C is confirmed by a low-abundance MS fragment combined with infrared spectroscopy at $m/z=44$, 92, 31 and 41, respectively [10,28–30]. The MS fragments for small silicane ($m/z=46$, 60) and methane ($m/z=16$) are detected during 400–800 °C in addition to the reappearance of CH_3NH_2, and CH_3CN [23,31]. According to the results of IR–MS, the mass losses during pyrolysis process are mainly related to the escape of CH_3NH_2 and CH_3CN produced by polycondensation reactions and the release of CH_4 from the depolymerization of mixture precursor at high temperature. As shown in Fig. 4, the final Si–B–C–N ceramics prepared at 1200 °C and 1500 °C show predominant FTIR peaks at 799, 1075 and 1378 cm^{-1}, which are typical absorption bands of Si–C, Si–N and B–N [32,33].

The microstructures of the ceramics prepared by annealing the pyrolysis product from P2 at 1800 °C are characterized by SEM and TEM (Fig. 5). Low-magnification SEM image (Fig. 5a) shows that the ceramics are dense. The inset image demonstrates that the ceramics consist of fine and equiaxed grains. Fig. 5b illustrates a fracture of the ceramics, indicating a homogeneous composition which is a typical character of precursor-derived ceramics. The TEM image (Fig. 5c) reveals that the sample consists of crystal grains (label 1) with turbostratic structure (label 2). The EDX results indicate that the grain and grain boundary are composed of Si and C, B, C and N elements, respectively (Fig. 5d and e). The weak signal of O comes from the oxidation of mixture precursor during operation. For the crystallization during pyrolysis process and the grain growth during annealing treatment, the presence of B–C–N phase hinders the atomic diffusions, retards the growth and so that limits the grain size of SiC crystals, which is in agreement with literature [34].

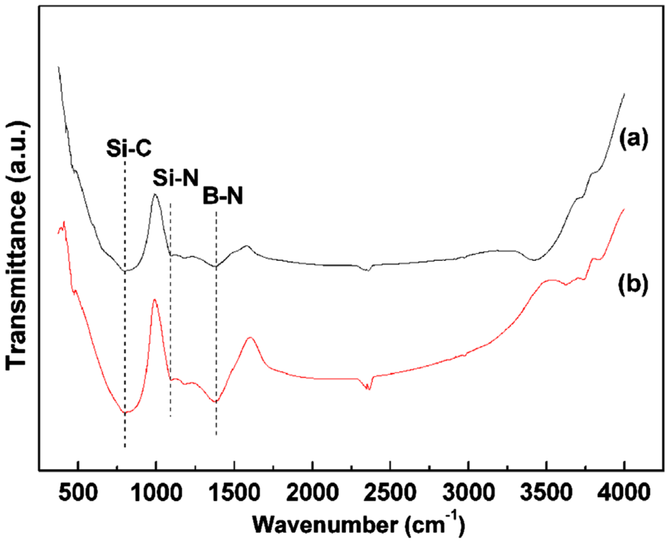

Fig. 4. FTIR spectra of pyrolyzed Si–B–C–N ceramics from P2 at (a) 1200 and (b)1500 °C.

To study the crystallization behavior, the prepared ceramics were annealed subsequently at 1450–2200 °C. XRD results of the annealed samples are shown in Fig. 6. It can be seen that the as-pyrolyzed ceramics are amorphous at 1450 °C and the crystallization starts at about 1550 °C. Very broad diffraction peaks indicate the small size (even nanoscale size) of the grains, which is consistent with the SEM observation shown in Fig. 5a. When the annealing temperature increases to 1600 °C and 1800 °C, no noticeable change is observed for the intensity and configuration of the diffraction peaks. Silicon nitride (β-Si_3N_4) phase and h-BN phase appear besides β-SiC and C phases when the sample is further annealed at 2000 °C and 2200 °C.

The thermal stability of the as-pyrolyzed Si–B–C–N ceramics was investigated by annealing the ceramics at different temperatures for 1 h in argon, as is shown in Fig. 7. From 1000 °C to 1500 °C, there is a slight mass loss of about 0.6%, which is attributed to the further pyrolysis of residual polymer in the as-pyrolyzed ceramics. The mass loss of 0.9% between 1500 and 1800 °C is caused by the vaporization of SiO (Eq. (1)) since trace oxygen remains in the ceramics (Fig. 5e). Hence, the sample only have a total weight loss of about

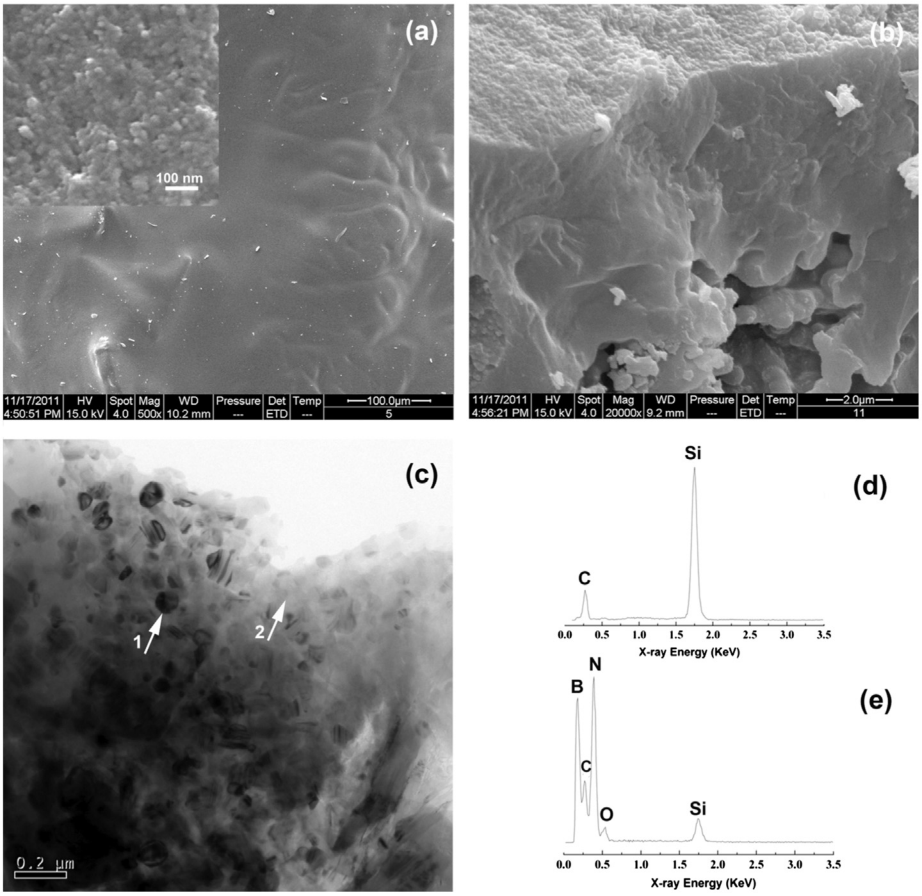

Fig. 5. The electron microscopy characterization of the Si–B–C–N ceramics annealed at 1800 °C pyrolyzed from P2. (a) SEM image of the surface of ceramics. The inset shows the magnified image of the surface. (b) SEM image of the fracture of the ceramics. (c) TEM image of the ceramics. The grain and grain boundary are labeled with 1 and 2, respectively. (d) and (e) EDX results of the grain and grain boundary phase.

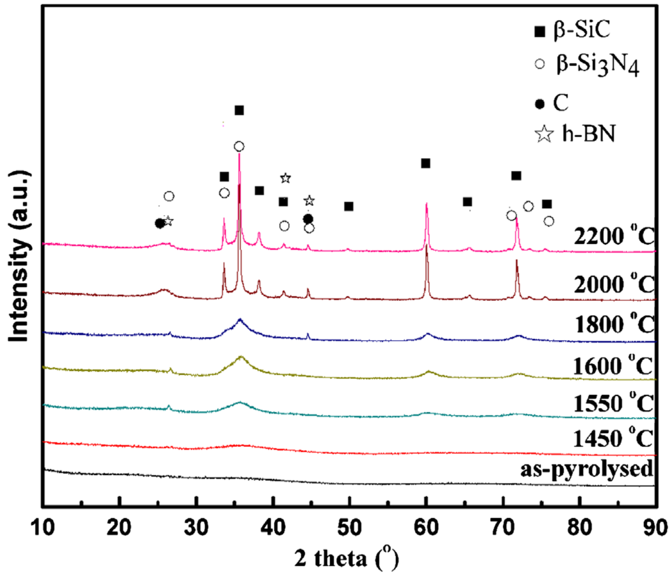

Fig. 6. XRD patterns of as-pyrolyzed Si–B–C–N ceramics from P2 and the ceramics annealed at different temperatures in argon atmosphere.

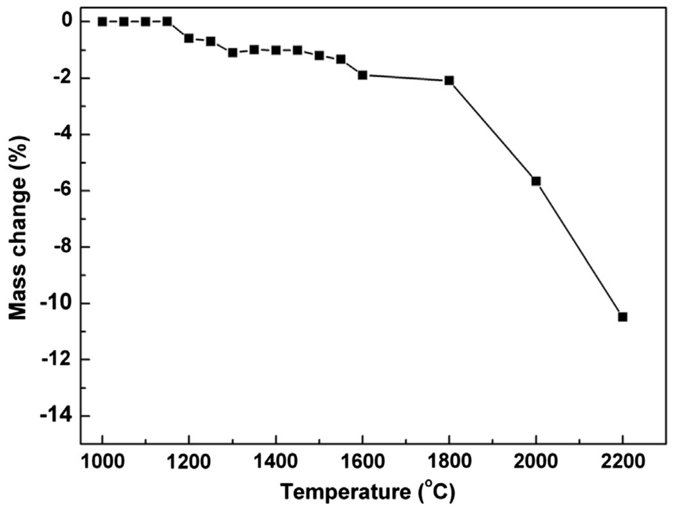

Fig. 7. Mass changes analysis of the Si–B–C–N ceramics from P2 after annealing at high temperatures in argon atmosphere.

2.08% until the temperature reaches to 1800 °C, indicating the excellent thermal stability of the ceramics in argon. When the temperature further increases to 2000 °C, decomposition reaction occurs. Dramatic mass losses of 3.5% from 1800 to 2000 °C and 4.8% between 2000 and 2200 °C are observed, which are attributed to the escape of N_2 generated by the reaction between carbon and Si_3N_4 and the decomposition of Si_3N_4 (Eqs. (2) and (3)) [35]. These results are also in good accordance with the XRD results shown in Fig. 6. Therefore, the formation of Si_3N_4 phase at high annealing temperature is believed to be one of the most important factors for the excellent high-temperature stability of the Si–B–C–N ceramics. The main reactions are proposed as follows:

$$SiO_2\ (s)+C\ (s)\rightarrow SiO\ (g)+CO\ (g)\quad \Delta G_{1800\,^\circ C}=-13.25\ \mathrm{kJ\ mol^{-1}} \tag{1}$$

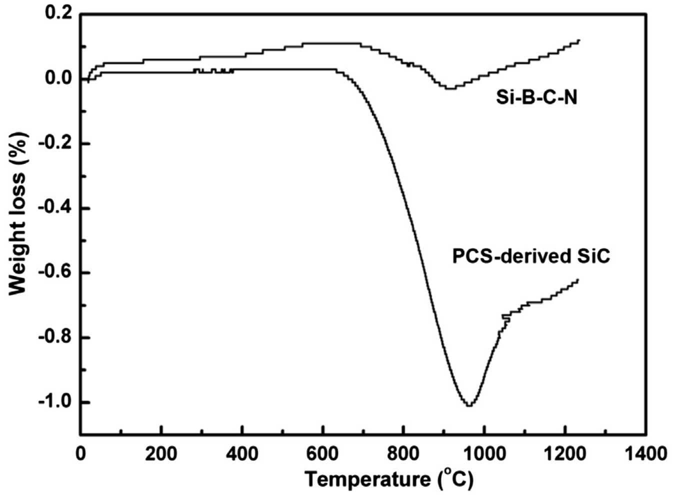

Fig. 8. TG curves of PCS-derived SiC ceramics and P2-derived Si–B–C–N ceramics in air.

$$Si_3N_4\ (s)+3C\ (s)\rightarrow 3SiC\ (s)+2N_2\ (g)\quad \Delta G_{2000\,^\circ C}=-163.11\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

$$Si_3N_4\ (s)\rightarrow 3Si\ (g)+2N_2\ (g)\quad \Delta G_{2000\,^\circ C}=-2.57\ \mathrm{kJ\ mol^{-1}} \tag{3}$$

The outstanding thermal stability of quaternary Si–B–C–N ceramics was ascribed to the formation of turbostratic BN that could act as a diffusion barrier for atoms, which could restrain the formation of crystalline phase or slow down related decomposition reactions [36].

The thermal stability of the as-pyrolyzed Si–B–C–N ceramics in air was detected by TG, as is shown in Fig. 8. For comparison, the thermal stability of the SiC ceramics derived from PCS is also presented. It can be seen that the masses of both ceramics do not obviously change below 700 °C. However, the Si–B–C–N ceramic exhibits a slight weight loss from 700 to 950 °C and an obvious weight gain above 1000 °C. The slight weight loss of Si–B–C–N ceramics below 950 °C is due to the vaporization of CO_2, which is generated from the oxidation of free carbon in Si–B–C–N ceramic. The weight gain above 1000 °C is attributed to the oxidation of BN to B_2O_3 and SiC to SiO_2, which form a stable borosilicate glass above 372 °C [37]. The dramatic weight loss of SiC ceramic below 960 °C is due to the oxidation of free carbon to CO_2, while the weight gain above 1000 °C may be caused by the formation of SiO_2. Therefore, it can be seen that the anti-oxidation performance of Si–B–C–N ceramics is superior to that of SiC ceramics because the formation of a passivated amorphous oxide layer on Si–B–C–N ceramics restrains the diffusion-controlled oxidation.

4. Conclusions

Si–B–C–N ceramics with amorphous structure are successfully prepared by co-pyrolysis of PCS and PBN precursors. The addition of PBN precursor can weaken the crystallization of the Si–B–C–N ceramics. In addition, the Si–B–C–N ceramics exhibit excellent high-temperature thermal-stability, keeping amorphous structure up to 1800 °C in Ar and only has a little weight change up to 1300 °C in air. Obviously, this novel synthetic route to Si–B–C–N ceramics possesses advantages of convenient handling and high-efficiency, which paves a simple path to the fabrication of amorphous Si–B–C–N ceramics.

Acknowledgments

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