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Thermal stability and mechanical properties of SiC particulate-reinforced Si–C–N composites after heating at 2000 °C

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Abstract

A SiC particulate-reinforced Si–C–N ceramic composite was fabricated using the precursor impregnation and pyrolysis method, and its thermal and mechanical properties were analyzed. The weight loss of the composite was 5% after a heating at 2100 °C in Ar. The pores of the composite enlarged at and above 1700 °C in Ar due to the decomposition of the Si–C–N matrix. However, the composite retained mechanical properties such as strength and hardness after heating at 1700 °C. 88% of the original strength was remained after heating at 2000 °C for 10 h although the fabrication temperature was 1350 °C. The weight gain of the composite was 3.2% after an oxidation at 1450 °C for 30 min in air. The inner oxidation of the particulate-reinforced composites (PRC) was suppressed above 1400 °C due to the closure of the open pores by SiO_2. Consequently, the composite possessed excellent creep resistance at 1400 °C in air. The SiC/Si–C–N composite is a challenging candidate for the application at high temperature.

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1. Introduction

Under defined conditions ceramics derived by the pyrolysis of Si-based polymers can provide excellent thermal, chemical and mechanical stability at rather high temperatures.[1] Consequently, intensive research efforts have been performed during the last two decades for the fabrication of such precursor-derived ceramic materials in the form of monoliths,[2] coatings,[3] fibers,[4] and composites.[5]

The precursor impregnation and pyrolysis (PIP) method has been investigated for the fabrication of precursor-derived ceramic composites.[6] In the PIP method, woven fiber fabrics are impregnated with a liquid precursor using the vacuum or pressure casting method, and the impregnated precursor is cross-linked by heat or UV light. Subsequently, the composites are pyrolized at 1000–1400 °C. Because of the degassing and shrinkage of the precursor during pyrolysis, the impregnation and pyrolysis cycles must be repeated several times to obtain sufficiently dense composites.[7] Accordingly, filler materials such as SiC have been used to decrease the number of the processing cycles by minimizing the free space where precursor-derived ceramics should be filled.[8]

The thermal stability of polymer-derived Si–C–N ceramics is reported to be maintained up to 1450 °C. Above this temperature a carbothermal reaction of Si–N units occurs which is accompanied with the crystallization of SiC/Si_3N_4 or SiC/C and the loss of molecular nitrogen.[9] However, the addition of filler powder to ceramic precursors can have beneficial effects to the processing of precursor-derived ceramics.[5] SiC particulates are expected to improve the high temperature properties of the resultant composites because SiC does not decompose at 2100 °C in an oxygen-free environment.[10,11] In addition, the application of such filler reduces the amount of the costly and thermally less stable Si–C–N precursor within ceramic components.

In the present investigation, a Si–C–N-based precursor was used to fabricate SiC particulate-reinforced composites (PRC) using the PIP method. Mechanical properties and high temperature stability of the resultant ternary composite material were evaluated up to 2000–2100 °C.

2. Experimental procedure

SiC powder (A 10, H. C. Starck, mean particle size (d_{50}): 0.51 μm) was selected as the filler material for the manufac-

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ture of the particulate-reinforced composites. The particle size of the filler decreased further by planetary milling for 5 h with isoprophyl alcohol, SiC ball and SiC jar. The slurry was dried at 70 °C for 24 h while stirring. The dried powder was sieved and compacted by cold isostatic pressing (400 MPa) into cylindrical pellets (diameter: 1.4 cm, height: 4 mm). The pellets were heat-treated at 1750 °C for 2 h in Ar (0.15 MPa) in order to remove surface SiO_2.[12] The heat-treated powder compacts were then impregnated with a commercially available polysilazane (VL 20, KION) which was diluted with tetrahydrofuran (1:1 by volume) to decrease its viscosity. The impregnation of the precursor solution into the heat-treated SiC pellets within a metal mold was performed by vacuum infiltration. Then, the solvent of the precursor solution was removed under a reduced pressure (2×10^{-4} MPa) at 40 °C for 6 h. The mold was finally capped, put into a sealed metal container and heated for 6 h at 430 °C in order to cross-link the precursor polymer.[12] The entire sample preparation was performed in an inert gas glove box (Ar) to prevent any contact with air.

For pyrolysis the specimens were heated at 1350 °C in flowing Ar using a heating rate of 5 °C/min and were held at this temperature for 2 h. In order to avoid oxygen contamination during pyrolysis, high purity argon (Argon 4.8, Messer, >99.998 vol%) which passed through a gas purification system (oxisorb®, Messer) was used. The impregnation and pyrolysis cycle was repeated six times in order to increase the relative density of the PRC. The bulk density was determined after each PIP cycle by measuring the weight to volume ratio.

The mass loss and ceramic yield during the pyrolysis of the precursor with and without the SiC filler were monitored over a temperature range of 25–1450 °C (Ar, heating rate: 5 °C/min) by thermogravimetric analysis (TGA, Netzsch STA 409C). The weight change of the bulk Si–C–N, Si–C–N powder and $SiC_{filler}/Si–C–N_{matrix}$ PRC was monitored up to 2100 °C in Ar using a Netzsch STA 501 with a heating rate of 3 °C/min whereas in air the value was determined during heating (3 °C/min) and holding at 1450 °C for 30 min using a Netzsch STA 409C.

The mechanical properties of the PRC were investigated before and after a heating at 1700, 1900 or 2000 °C for 10 h in Ar. During heating, the samples were placed in a silicon carbide powder bed.[13] The weight change of the specimens was measured after heating, and the surface area of the heated specimens was analyzed by BET measurement (Brunauer, Emmett & Teller, Gemini, Micrometrics). The as-obtained PRCs were plasma-etched (PT7150, Bio-rad, etching condition: 100 W, 13.56 MHz, $CF_4 + 33\%\ O_2$ mixture gas, 5 min, chamber pressure: 5.3×10^{-2} mbar) and were observed by scanning electron microscopy (SEM) equipped with Schottky field emitter (DSM 982, Zeiss).

The fracture strength of the PRC was measured using disc-shaped specimens (10 mm in diameter and 200–300 μm in thickness with one face polished to 1 μm finish) by the "ball on three balls" method without additional polishing after heating up to 2000 °C.[14] Subsequently, the fractured surface was observed by SEM. The Young's modulus, hardness and fracture toughness of the PRC before and after heating was determined by using a resonance frequency and damping analyzer (IMCE RFDA system 23, Diepenbeek, Belgium) and Vickers indentation method (Micromet, Buehler). The phase composition of the specimens before and after heating was analyzed by X-ray diffraction (D 5000, Siemens) using Cu $K_{\alpha1}$ radiation.

For creep test, the PRC samples were machined into bars ($2 \times 2 \times 8\ mm^3$). A compressive stress of 100 MPa was applied for 60 h in air at temperatures of 1300, 1350 or 1400 °C (DSM 6101, Amsler). The microstructure and oxidation of the samples were analyzed subsequently by SEM and energy dispersive X-ray spectroscopy (EDX, Inca-energy, Oxford).

3. Results and discussion

3.1. Thermal stability

Fig. 1 illustrates the density of the PRC as a function of the number of impregnation/pyrolysis cycles. The densification was mostly completed after the fourth cycle. A ceramic yield of 82.7% was determined by TGA analysis (data not shown). The chemical composition and true density of the Si–C–N was $SiC_{0.68}N_{0.91}$ and 2.56 g/cm^3.[10]

Fig. 2 displays weight changes of the specimens in Ar up to 2100 °C. The decomposition of the Si–C–N ceramics started at 1450 °C due to the carbothermal reaction of Si–N units or silicon nitride;[9]

$$Si_3N_{4(s)} + 3C_{(s)} \rightarrow 3SiC_{(s)} + 2N_{2(g)}. \quad (1)$$

The total weight loss of the bulk Si–C–N and Si–C–N powder was 27.7 and 26.4% at 2100 °C, whereas the SiC/Si–C–N PRC lost only 5% of its original mass (Fig. 2(c)) because SiC is thermally stable at 2100 °C.[9] The weight loss of the Si–C–N matrix within the PRC was estimated to be 24.6% by considering the weight ratio between the filler and the matrix. The mass loss of the Si–C–N within the PRC was smaller than that of the bulk Si–C–N. The average pore diameter of an as-fabricated SiC/Si–C–N PRC was 16 nm.[10] Gas permeability in a porous media was reported to be inversely proportional to the square of its average pore diameter.[15] During the TGA measurement, the nitrogen partial pressure within the PRC is believed to increase

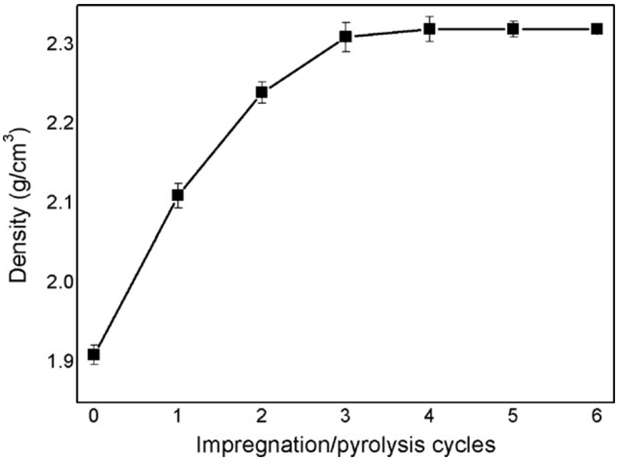

Fig. 1. Apparent density of the PRCs *vs.* number of impregnation/pyrolysis cycles.

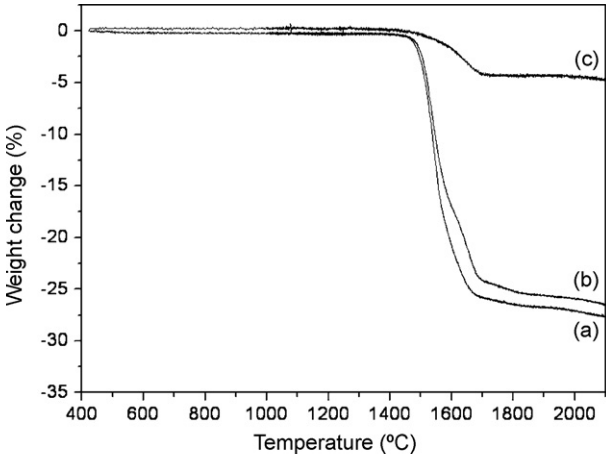

Fig. 2. High temperature thermogravimetric analyzes of (a) bulk Si–C–N, (b) Si–C–N powder (d_{50}: 10.8 μm, specific surface area: 1.75 m^2/g) and (c) SiC/Si–C–N PRC (specific surface area: 9.1 m^2/g). Measurement condition: Ar, gas flow rate: 100 ml/min, heating rate: 3 °C/min.

Table 1
Selected properties of the composite materials investigated before and after additional post heat treatment.

	As-fabricated	After heating (10 h in 0.1 MPa Ar)		
		1700 °C	1900 °C	2000 °C
Weight loss (%)	–	5.5	7.2	7.8
Density (g/cm^3)	2.4	2.2	2.2	2.2
Surface area (m^2/g)	9.1	3.7	1.1	1.2
Bending strength (MPa)	357 ± 45	373 ± 27	323 ± 33	314 ± 40
Vickers hardness (GPa)	8.0 ± 0.3	7.8 ± 0.3	3.6 ± 0.2	3.3 ± 0.4

by reaction (1) and the slow ventilation from the composite. As a result, the decomposition of the Si–C–N matrix within the PRC is believed to be suppressed. The thermal stability of the PRC was higher than that of the monolithic Si–C–N due to the high refractoriness of SiC and small pore size.

Table 1 summarized the weight loss, density and surface area of the composites before and after heating. The weight loss of the SiC/Si–C–N PRC was 5.5% after heating at 1700 °C for 10 h in Ar. The value increased slowly up to 2000 °C. Likewise, the density decreased after heating at 1700 °C by the decomposition of the Si–C–N. However, the value did not strongly change above this temperature because the mass loss was mostly fin-

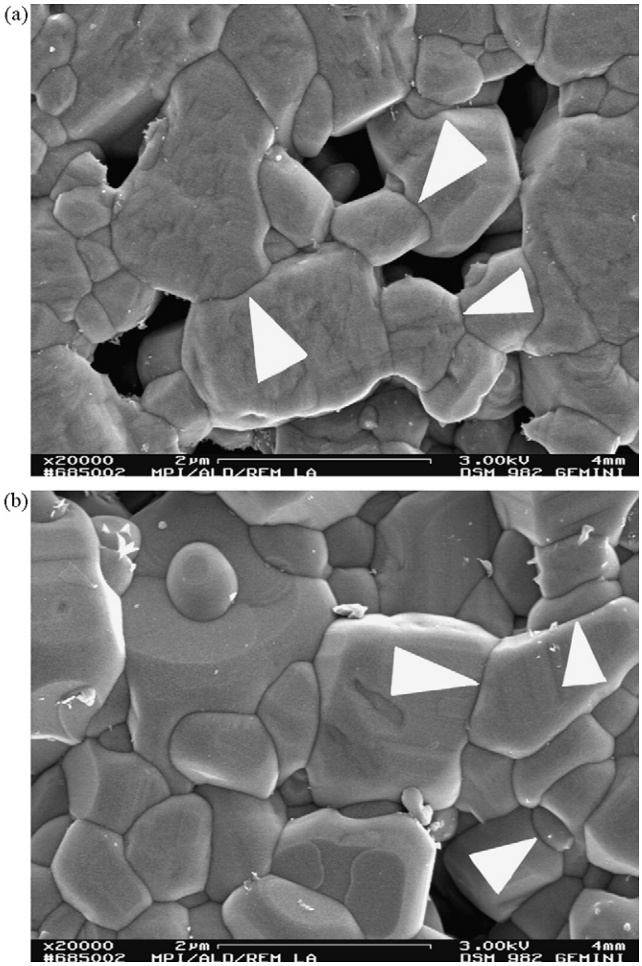

Fig. 3. Microstructure of the plasma-etched SiC/Si–C–N PRC after heating at 1700 °C and (b) 1900 °C (◄: necks formed between the filler particulates).

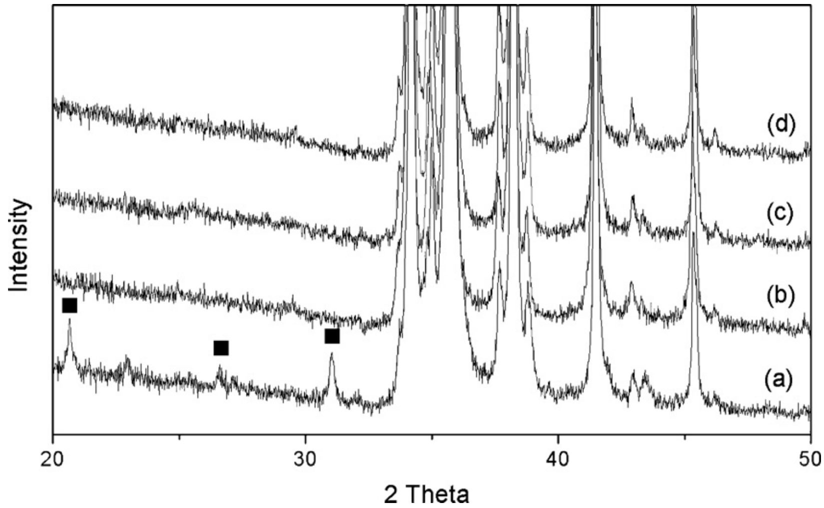

Fig. 4. XRD patterns of the SiC/Si–C–N PRC (a) before and after heating for 10 h in 0.1 MPa Ar at (b) 1700, (c) 1900 and (d) 2000 °C. (■: Si_3N_4, others: SiC).

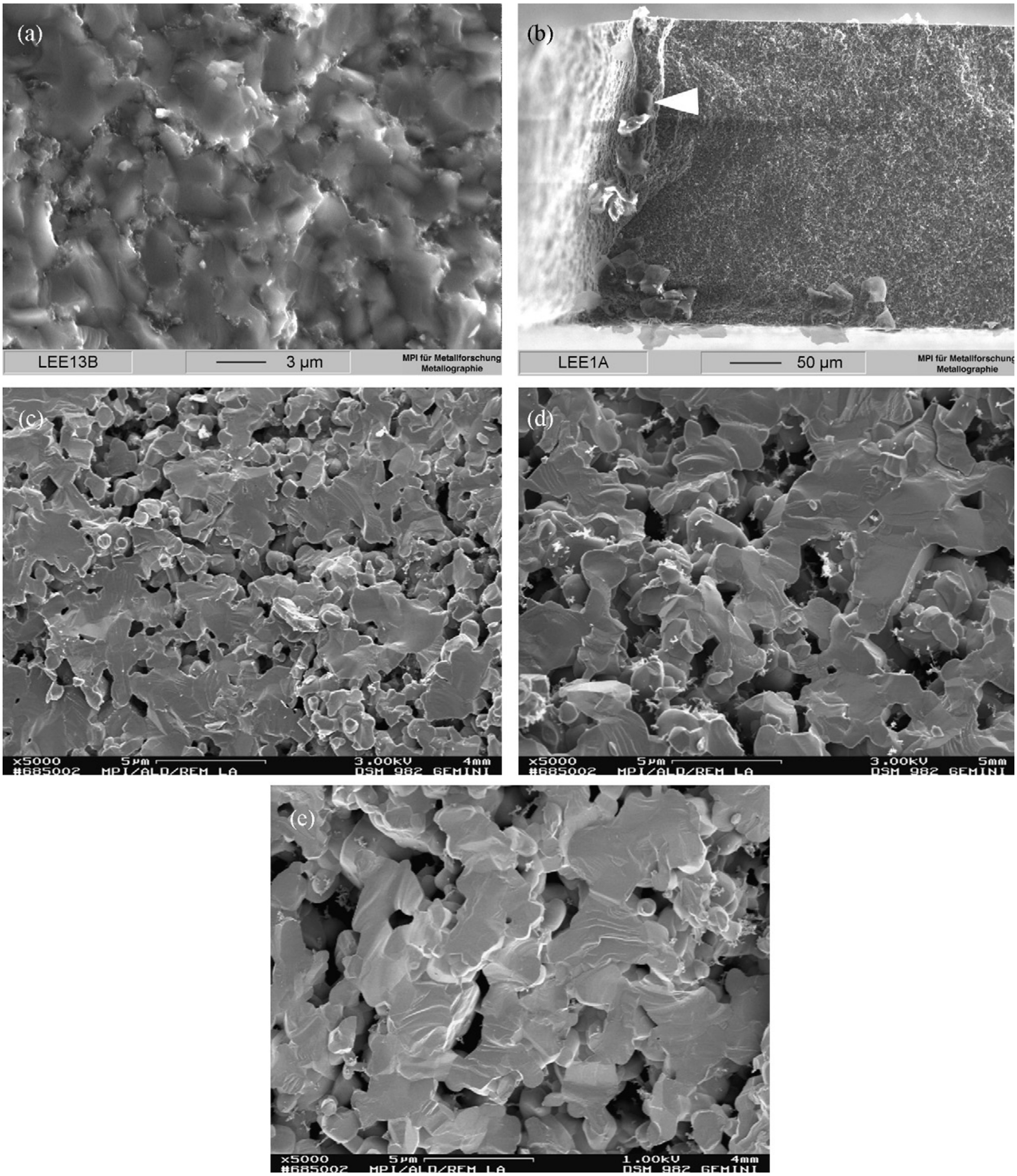

Fig. 5. Fractured surface of the PRC. (a), (b) as-fabricated specimens (◀: fracture origin), and after heating for 10 h in Ar at (c) 1700, (d) 1900 and (e) 2000 °C.

ished as shown in Fig. 2(c). In addition, the neck formation and partial densification of the SiC particulates occurred at and above 1700 °C (Fig. 3), which compensated for the decrease of the density caused by the mass loss.

The surface area of the as-fabricated composite was 9.1 m^2/g. The value decreased above the pyrolysis temperature, which became distinct at 1900 °C (1.1 m^2/g). The growth of SiC crystallite with increasing temperature was reported to be one of the reasons.[16] The neck formation and smoothing of the filler particulates are considered as the other reasons (Fig. 3(a) and (b)).

The X-ray diffraction patterns indicated the presence of silicon carbide (Fig. 4) which for the most part originated from the filler material. The reflections of silicon nitride were also observed in the as-fabricated PRC (Fig. 4(a)), indicating that the crystallization of the Si–C–N matrix occurred during the pyrolysis at 1350 °C.[17] The nitride was not identified after heating the specimens at and above 1700 °C due to reaction (1) (Fig. 4(b)). The XRD data did not distinctly change above 1700 °C (Fig. 4(c)–(d)) because the heated PRCs were mainly composed of thermally stable SiC after the decomposition. Schmidt et al. observed a nearly complete crystallization of an amorphous Si–C–N into SiC after a heating at 1645 °C for 1 h.[18]

The microstructure of the composite was revealed from the fractured surface. Transgranular fracture was the major fracture mode in all cases (Fig. 5). The Si–C–N matrix filled the space in between the SiC particles (Fig. 5(a)). Pores were formed after heating at 1700 °C, the size of which increased and the number decreased at and above 1900 °C (Fig. 5(c)–(e)). The formation and enlargement of the pores were mainly caused by the decomposition of the ternary ceramic matrix and the crystallization and growth of SiC within the amorphous Si–C–N. Due to the large difference of density between the Si–C–N and SiC (2.56 *vs.* 3.22 g/cm^3), the crystallization creates additional porosity.

3.2. Oxidation behavior

Fig. 6 shows the TGA data of the Si–C–N bulk precursor-derived ceramics, the Si–C–N powder compact and the PRC in flowing air. The bulk Si–C–N showed a high oxidation resistance up to 1450 °C. The overall weight gain was less than 0.5% (Fig. 6(a)). A weight loss started at 700 °C upon heating, which was followed by a weight gain above 1050 °C. The mass gain slowed down above 1200 °C. This behavior was in agreement with the findings of Bahloul et al., who reported that the oxidation of Si–C–N ceramics could be divided into three stages.[19] The weight loss in the first stage was due to an oxidation of free carbon, and the weight gain in the second stage was attributed to the formation of silica. The oxidation reduced the open porosity due to the volume expansion during the conversion of Si–N–C and SiC into SiO_2 (linear expansion of $SiC_{0.6}N_{0.9}$: 36%), which inhibited the inner oxidation at the third stage.[20,21]

The Si–C–N powder compact revealed a continuous weight gain up to 1450 °C because interior oxidation proceeded even at high temperature presumably due to the presence of large pores (Fig. 6(b)).

The onset temperature of the first and second stage of the PRC was similar to those of the Si–C–N powder compact (Fig. 6(c)). However, the PRC had the third stage at about 1400 °C. Different from the Si–C–N powder compact, the open pores of the PRC could be nearly completely closed at this temperature due to the small pore size. The mass gain by inner oxidation was strongly suppressed during the testing at 1450 °C for 30 min. The overall weight gain of the PRC was 3.2%.

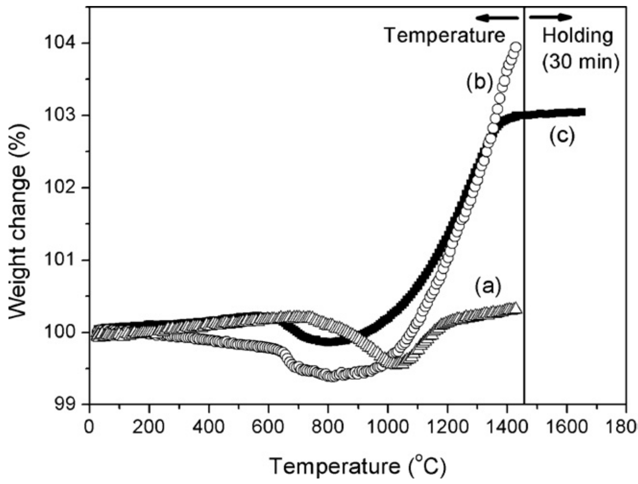

Fig. 6. Thermogravimetric analyzes up to 1450 °C in air (heating rate: 3 °C/min, flow rate: 100 ml/min). (a) Bulk Si–C–N, (b) Si–C–N powder and (c) SiC/Si–C–N PRC. (30 min holding at 1450 °C in the case of the PRC).

3.3. Mechanical properties

The bending strength, Vickers hardness, Young's modulus and fracture toughness of the as-prepared PRC were 357 MPa, 8.0 GPa, 137 GPa and 2.7 MPa m$^{1/2}$ (Table 1). The strength increased after heating at 1700 °C. The beneficial effect of the neck formation as shown in Fig. 3(a) was believed to be more important than the undesirable effect caused by the enlargement of the pores at this condition. However, the strength decreased after heating at 1900 °C and above, indicating that the property was more strongly affected by the enlargement of the pores. The composite retained 88% of the original strength after heating at 2000 °C for 10 h in Ar although the processing temperature of the PRC was 1350 °C. Rice pointed out that the hardness and Young's modulus of ceramics are strongly affected by porosity, while their strength was mainly governed by the size and shape of large surface flaws.[22] By using the simple Griffith equation, the strength of the material under consideration was calculated to be 830 MPa when the fracture toughness of the sample was 2.7 MPa m$^{1/2}$ and a semi-circular crack with 10 μm depth was considered as the fracture origin.[23] Because the strength of the PRC was smaller than this value, pores with 1–5 μm in size shown in Fig. 5(d) and (e) were not considered as the reason for the decrease of the strength. Large flaws of >10 μm in size, as shown in Fig. 5(b), behaved as the fracture origin. Presumably, the size of the strength-controlling flaws also increased by the decomposition of the matrix phase during the heating at 1900–2000 °C.

The hardness of the PRC decreased after heating at 1900 °C compared to the value at 1700 °C although the density values were similar between the specimens (Table 1). The hardness of porous ceramics is strongly affected by their porosity.[22] However, the deterioration of the composites in this research was not mainly originated from the increase of porosity. The crystallization and growth of SiC crystals within the amorphous Si–C–N matrix was believed to be the main reason. The crystallization of amorphous precursor-derived ceramics was reported to induce the deterioration of the material due to the formation of pores and cracks.[24] Ziegler et al. reported the reduction of hardness after heating of a Si–C–N at 1550 °C.[25] In contrast, the SiC/Si–C–N PRC retained the property at 1700 °C in this research. The hard SiC network shown in Fig. 3(a) is believed to sustain the structure of the PRC and the relatively soft Si–C–N matrix probably suppressed the movement of the SiC network against stress by filling the free spaces. After heating at 1900 °C, however, the matrix could not effectively suppress the movement of the SiC due to the strong deterioration and pore formation.

The compressive creep data of the PRC at 1350 °C are shown in Fig. 7. The total strain was 0.2% after 60 h of loading under 100 MPa pressure in air. The value increased slightly with tem-

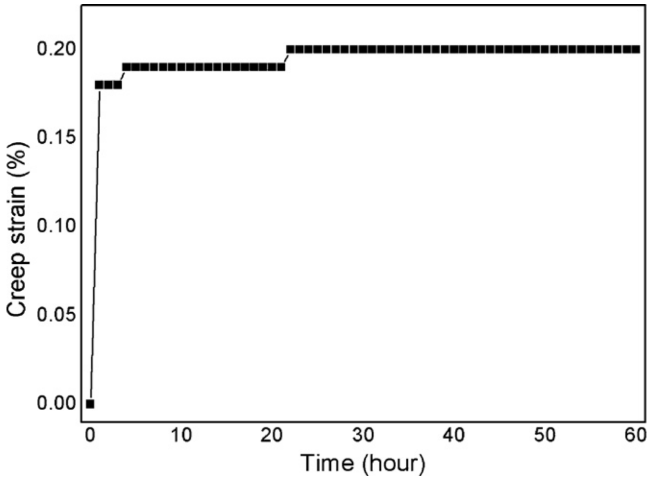

Fig. 7. Creep strain of the PRC at 1350 °C in air (loading: 100 MPa). The data were taken at each hour.

Table 2
Compressive creep strain after testing for 2×10^5 s under 100 MPa at different temperatures in air.

Temperature (°C)	1300	1350	1400
Strain (%)	0.15	0.20	0.21

perature up to 1400 °C (Table 2). Thurn et al. reported that the compressive creep strain of an as-prepared Si–C–N was 1.5% after a compressive creep test at 1400 °C for 2 h under 100 MPa pressure in air.[26] They improved the property to ∼0.2% after the testing for 60 h, but only after an intensive annealing treatment at 1400 °C for 300 h. The high creep resistance of the PRC prepared in the present investigation was attributed to the rigid SiC particle network in the more plastic Si–C–N matrix. Fig. 3 clearly shows the direct contact of the SiC filler particulates and the formation of rigid network. The relatively soft Si–C–N matrix may not directly contribute to the high creep resistance of the PRC, but most probably it suppressed the deformation of the rigid SiC filler particulate network during creep testing by filling the free spaces in between the network and sharing the stress applied to the network.

Fig. 8 shows the microstructure of the composite after the creep test in air. EDS data indicated that the gray areas as well as the enlarged pores shown in Fig. 8(a) were filled with SiO_2 (Fig. 8(b)). The oxidized area was thicker than 60 μm (Fig. 8(c)). Because the creep resistance of SiO_2 is much lower than that of SiC, the creep deformation of the PRC should increase in case the oxidation affected the creep behavior of the composite. However, the inner oxidation of the PRC during the creep test did not have a strong impact on the creep property because the

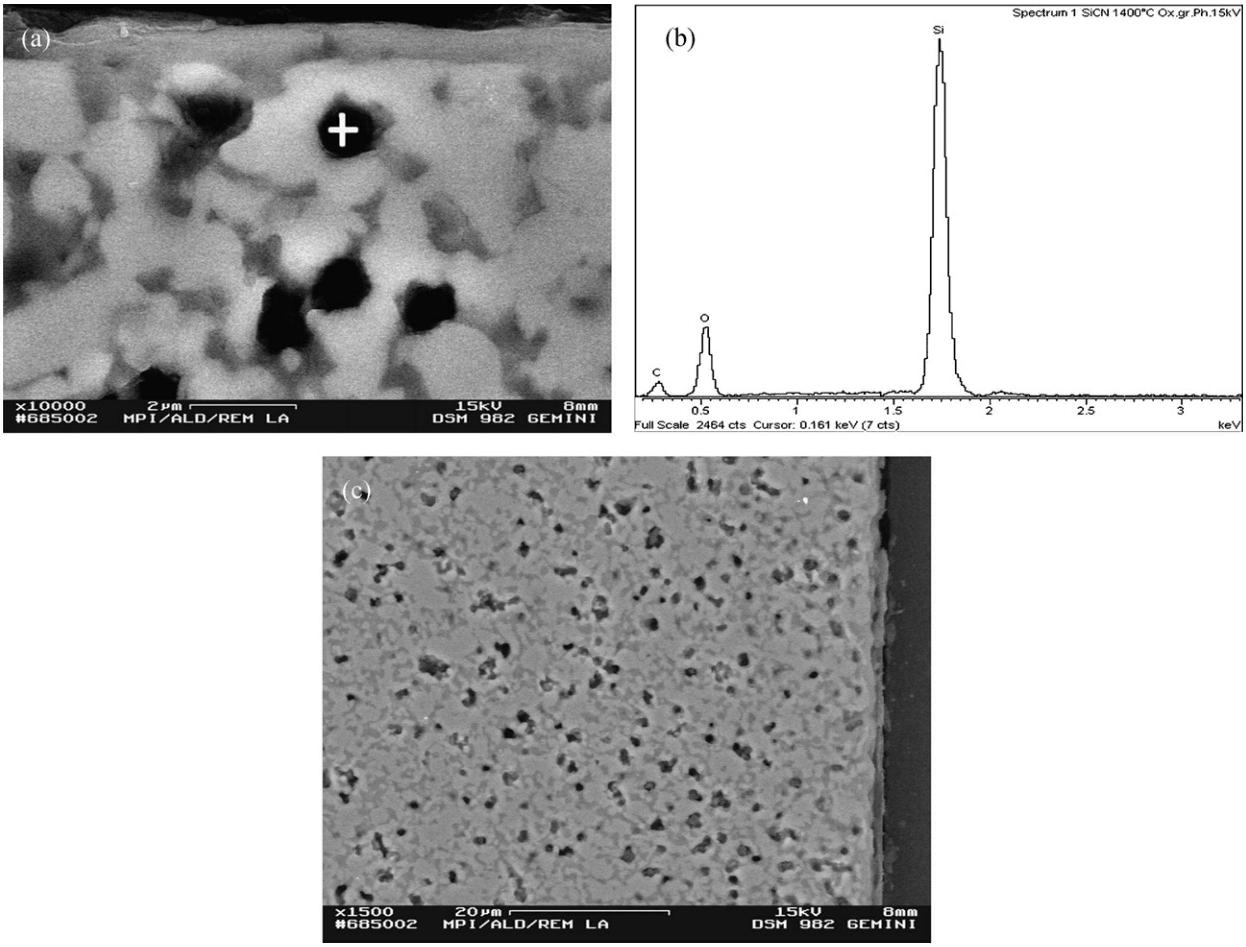

Fig. 8. Back scattered image of the PRC after the creep test at 1400 °C for 60 h under 100 MPa pressure. (a) ×10,000, (b) EDS data and (c) ×1500.

oxidation was effectively suppressed by the closure of the open pores as shown in Fig. 6(c).

4. Summary and conclusions

The SiC/Si–C–N PRC was thermally more stable than the monolithic Si–C–N due to the highly refractory filler particulates and small pore size. The total weight loss of the composite was 5% after heating at 2100 °C. The inner oxidation of the PRC decreased at 1400 °C due to the closure of open pores by SiO_2 which had formed during oxidation. The weight gain of the PRC did not strongly occur at 1450 °C once the pores were closed. The PRC retained 88% of the strength after heating at 2000 °C for 10 h. The pores of the PRC grew after heating at 1700 °C, but the decrease of strength and hardness became distinct at 1900 °C. The formation of pores and the growth of SiC crystals in the Si–C–N matrix were considered as the reasons. The PRC showed excellent creep resistance at 1400 °C in air (0.2%). The results clearly demonstrate that the SiC/Si–C–N PRC is a possible candidate for the application at high temperature.

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