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Fabrication of continuously porous SiC–Si_3N_4 composite using SiC powder by extrusion process

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Abstract

Large amounts of waste SiC sludge containing small amounts of Si and organic lubricant were produced during the wire cutting process of single crystal silicon ingots. Waste SiC sludge was purified by washing it with organic solvent and purified SiC powder was used to fabricate the continuously porous SiC–Si_3N_4 composites, using an extrusion process, in which carbon, 6 wt% Y_2O_3 + 2 wt% Al_2O_3 and ethylene vinyl acetate were added as a pore-forming agent, sintering additives and binder, respectively. In the burning-out process, the binder and carbon were fully removed and continuously porous SiC–Si_3N_4 composites were successfully fabricated. The green bodies containing waste SiC, Si powder and sintering additives were nitrided at 1400 °C in a flowing N_2 + 10% H_2 gas mixture. The continuously porous composites contained SiC, α-Si_3N_4, β-Si_3N_4 and few Fe phases. The pore size of the second passed and third passed SiC–Si_3N_4 composites was 260 μm and 35 μm in diameter, respectively. The values of bending strength and hardness in the second passed and third passed samples were 62.97 MPa, 388 Hv and 77.82 MPa, 423 Hv, respectively.

Keyword: Extrusion; Composites; Whiskers; Si_3N_4; Recycling; SiC

1. Introduction

Silicon carbide (SiC) is recognized as an important structural material because of its unique desirable properties, such as its high strength at high temperatures, and resistance to wear, corrosion and thermal shock.[1–4] To produce the Si wafer in the semiconductor industry, single crystal Si ingots were generally cut by the diamond wheel cutting process. In this case, large amounts of Si sludge were spontaneously generated by the sawdust of the single crystal Si ingots. To recycle waste Si sludge, reaction bonded Si_3N_4 (RBSN) ceramic composites were fabricated by the combination of nitridation and gas pressure sintering process.[5,6] However, recently, to reduce the Si loss as well as increase the production rate of Si wafers, the wire cutting process has been adopted. In this process also, large amounts of waste SiC powder are spontaneously generated due to the abrasion and fracture of large size SiC particles, but they cannot be reused in the wire cutting process due to the fine size of SiC particles. In attempts, to recycle this waste SiC sludge, there have been efforts made to produce the continuously porous SiC–Si_3N_4 composites as well as reaction bonded Si_3N_4 (RBSN) ceramics. There have been some advantages, such as the low price of raw powder and the low cost of production. Different types of sintering additives are commonly used in nonoxides ceramics, such as MgO, Al_2O_3, Y_2O_3 and other rare earth oxides or their combinations. Al_2O_3 and Y_2O_3 is one of the most common sintering additives to densify silicon carbide (SiC) ceramics.[7,8]

On the other hand, SiC ceramics are useable for industrial materials and environmental filter because of their unique material properties, especially at high temperatures. For use as an environmental filter, SiC ceramics should be porous, with a uniform size and distribution of pores as well as having excellent mechanical properties. Generally, the

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mechanical properties of porous bodies decrease as the porosity increase. Therefore, an innovative fabrication process is needed to make the continuously porous ceramics having superior mechanical properties. High fracture-toughened ceramic composites and high strength continuously porous ceramics can be fabricated using the extrusion process.[9–13] This process well control the fibrous microstructure of SiC ceramics by increasing the number of extrusion passes.

In this work, as a new approach, the continuously porous SiC–Si_3N_4 composites are fabricated by extrusion process. The different size of pores were prepared by increasing the number of extrusion passes without changing the sintering additives and Si is added to produce the reaction bonded Si_3N_4 (RBSN) in SiC matrix during the nitridation process.

2. Experimental procedure

Waste SiC sludge was washed with acetone to remove the organic agent followed by drying on a hot plate while stirring. Coarse particles were separated by sieving. Waste SiC powder, 5 wt% Si (H. Starck, average size: 2 μm) powder and sintering additives (6 wt% Y_2O_3, Daejung Chemicals & Metals Co., Korea-2 wt% Al_2O_3, Sumitomo Chemical Co., Japan) were homogeneously mixed in ethanol using a ball mill and Si_3N_4 balls as the milling media. The mixture was separated from the milling media and dried on a hot plate while stirring. Then, mixture powders (waste SiC powder, 5 wt% Si and sintering additives) were mixed with polymer, such as ethylene vinyl acetate 210 (ELVAX 210) and ethylene vinyl acetate 250 (ELVAX 250) by using a shear mixer. The granular-shaped polymer (ELVAX 210 and ELVAX 250) used as a binder and stearic acid ($CH_3(CH_2)_{16}COOH$, Daejung Chemicals & Metals Co., Korea) as a lubricant, were added to the chamber. The volume ratio of the ball milled mixture powders/polymer/stearic acid was 50/40/10. When the shear-mixing chamber was heated to 120 °C, the granular-shaped polymer was put into the chamber. After few minutes, the ball milled mixture powders were slowly added to the chamber. This homogeneous mixture was extruded to make filaments with a diameter of 3.4 mm. Extruded filaments were used to produce the tube by warm press. To make the rod, a pore-forming agent (carbon, Aldrich Chemical Company, USA) and polymer were also mixed with a shear mixer. The tube and rod combined together to prepare a feed roll and extruded to make the first passed filaments with a diameter of 3.4 mm as shown in Fig. 1. Binder burnout was performed in a tube furnace with a slow heating rate (45 °C/h) up to 700 °C in flowing air. The nitridation process was carried out at 1400 °C in flowing $N_2 + 10\%$ H_2 gas mixture for 20 h. The chemical analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS, Thermo Jarrell Ash Co., USA) and X-ray diffraction (XRD, D/MAX-250, Rigaku, Japan). Densities of nitrided samples were measured by the Archimedes method with an immersion medium of water. The average Vickers hardness was measured by indenting with a load of 2.5 kg (20 points/sample). To prepare the bending test samples, the nitrided samples having 3.4 mm in diameter were cut with 35 mm in length and each sample was polished with dia-

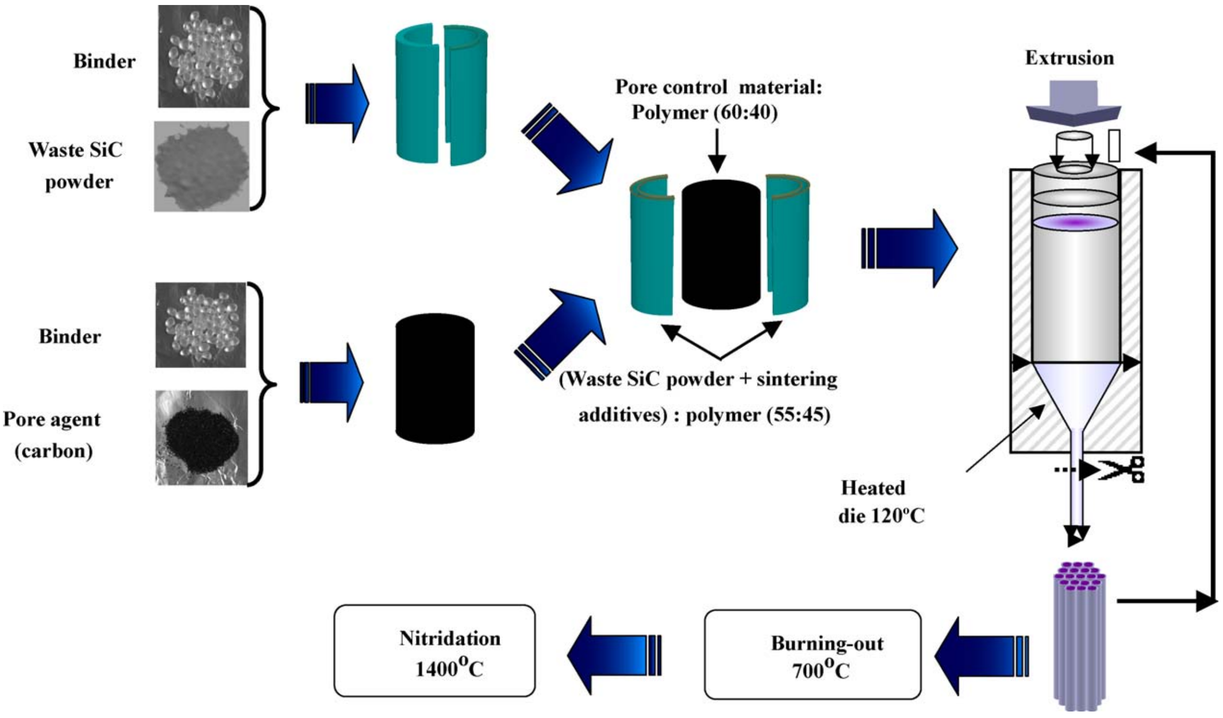


Fig. 1. Schematic diagram of extrusion process.

mond pastes up to 3 μm. The average bending strength was measured by three-point bending method with a span length of 10 mm and crosshead speed of 0.1 mm/min, using universal testing machine (Unitech^{TM}, R&B, Korea). The pore size, microstructure and crystal structure of the continuously porous SiC–Si_3N_4 composites were examined by scanning electron microscopy (SEM, JSM-635F, Jeol) with Pt coating and transmission electron microscopy (TEM, JEM-2010, Jeol) with C coating techniques.

3. Results and discussion

Fig. 2 shows the SEM micrographs and EDS profile of waste SiC powder. In Fig. 2(a), waste SiC powder has an irregular shape and an average particle size of about 7 μm in diameter. In Fig. 2(b), the enlarged SEM micrograph, fine Si particles of about 2 μm, which were attached during the wire cutting process of single crystal Si ingots, were observed on the surface of the SiC particles. Fig. 2(c), the EDS profile was taken from the rectangular region in Fig. 2(b). In the EDS profile, a small amount of Fe phase is detected as well as Si and C elements. The main reason for the detection of Fe is due to the wear loss of the cutting wire.

Table 1 shows the result of chemical analysis of waste SiC powder. In waste SiC powder, the content of Fe shows relatively high value of about 4.61 wt%. Waste SiC powder also contained small amounts of other impurities, such as Al, Ca, Cr, P and S.

Fig. 3 shows the TG and DTA profiles of waste SiC powder. The weight of waste SiC powder decreased up to 550 °C. Up to 550 °C, most of the organic agents attached on the surface of waste SiC powder were burned out and removed. Thus, the percentage of weight loss from room temperature to 550 °C was about 17%. However, above 550 °C, the weight of SiC powder increases as the temperature increases. The DTA profile shows an exothermic reaction at 550 °C, which may be due to the oxidation of Si particles.

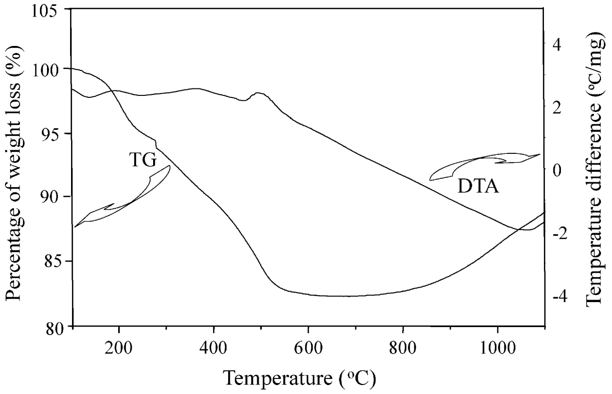


Fig. 3. TG and DTA profiles of waste SiC powder.

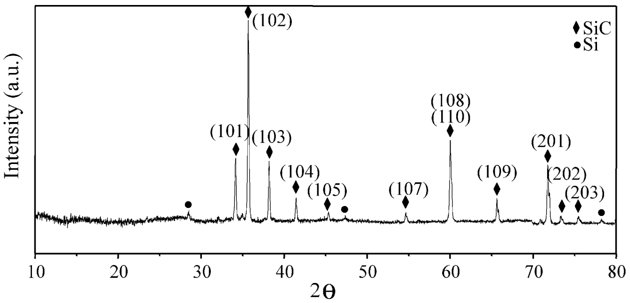


Fig. 4. XRD profile of waste SiC powder.

Fig. 4 shows the XRD profile of waste SiC powder. The main peaks are in the SiC phase although Si phase is detected as a minor phase. However, the impurity of Fe was not detected by XRD.

Fig. 5 is SEM micrographs showing the transverse (a–c) and longitudinal (d–f) sections of extruded bodies. Fig. 5(a) and (d) show the first passed transverse and longitudinal sec-

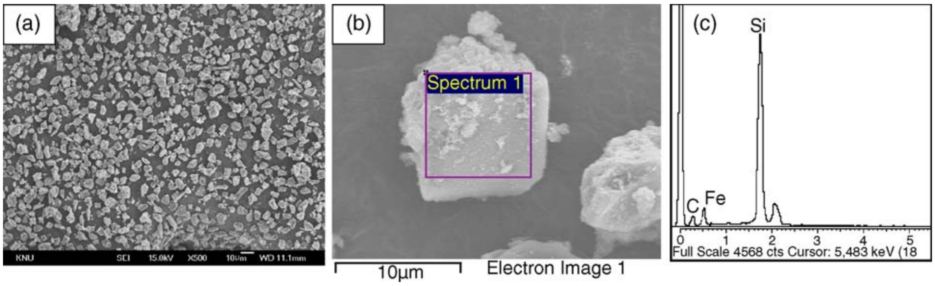


Fig. 2. Low magnification (a) SEM image; (b) enlarged image and (c) EDS profile of waste SiC powder.

Table 1
Chemical composition of waste SiC powder

	Element							
	Si	Fe	P	Zn	Al	S	Ca	Cr
SiC powder (wt%)	93.6	4.61	0.42	0.33	0.27	0.26	0.16	0.11

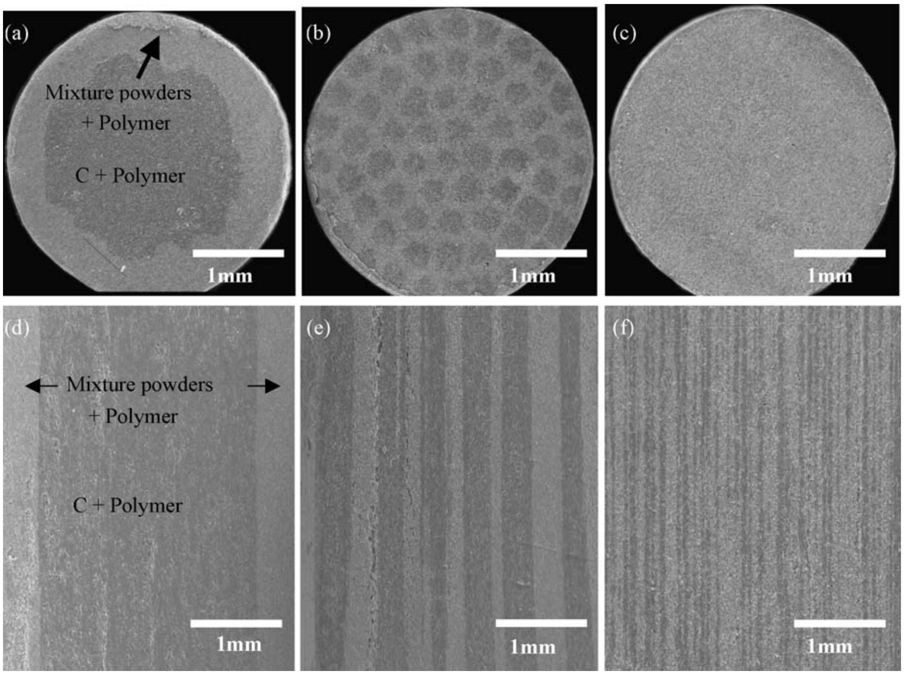


Fig. 5. SEM micrographs of transverse (a) first passed; (b) second passed; (c) third passed and longitudinal; (d) first passed; (e) second passed and (f) third passed of extruded bodies.

tion of extruded bodies, respectively. The core part of the first passed extrusion bodies is a pore-forming agent/polymer and the shell part shows ball milled mixture powders (waste SiC powder, 5 wt% Si, 6 wt% Y_2O_3–2 wt% Al_2O_3)/polymer. The diameter of the pore-forming agent and shell thickness of the first passed extruded bodies is 2.4 mm and 0.5 mm, respectively. The second passed filaments, which reloaded the first passed filaments into the die, were prepared using multi-pass extrusion process. The diameter of the pore-forming agent of the second pass-extruded bodies was approximately 265 μm. The third passed filaments (c, f) were also prepared in the same way by reloading the second passed filaments. The second passed filaments (b, e) show a homogeneous distribution and an alternative layer of the pore forming agent/polymer region (dark color) and ball milled mixture powders/polymer region (gray color) in both transverse and longitudinal sections, respectively. In the third passed filaments; the pore forming agent layers were very fine. The pore forming agent layer was remarkably decreased with the increase in the number of extrusion passes.

Fig. 6 shows the XRD patterns of waste SiC–5 wt% Si mixture powders (a) including sintering additives, (b) after burning out and (c) after nitridation of the SiC–Si_3N_4 bodies. After burning out, the phase change was not found. After nitridation at 1400 °C in flowing $N_2 + 10\%$ H_2 mixture gas, α-Si_3N_4 and β-Si_3N_4 phases were existed in the SiC matrix. However, Y_2O_3 peaks were not detected because sintering additives (6 wt% Y_2O_3–2 wt% Al_2O_3) were changed into an amorphous phase. During nitridation process, Si phase was directly transferred to reaction bonded Si_3N_4 due to the nitridation mechanism of compacted Si by the reaction of cracks and dislocation.[14,15] The intensity of α-Si_3N_4 peaks was strong while the β-Si_3N_4 peaks were weak. From no detection of Si peak using Cu Kα radiation with a Rigaku RAD-2C diffractometer, it is confirmed that Si powder was fully nitrided and transferred to α-Si_3N_4 and β-Si_3N_4 without any residue Si phase.

Fig. 7 shows the SEM micrographs of (a) the second passed; (b) the enlarged image of the second passed; (c) the third passed and (d) the enlarged image of the third passed nitrided SiC–Si_3N_4 bodies. After burning-out and nitridation process, the pore-forming agent was successfully removed and produced continuously porous SiC–Si_3N_4 composites. But inside of continuous pores, many whiskers as indicated with an arrowhead were clearly observed. The

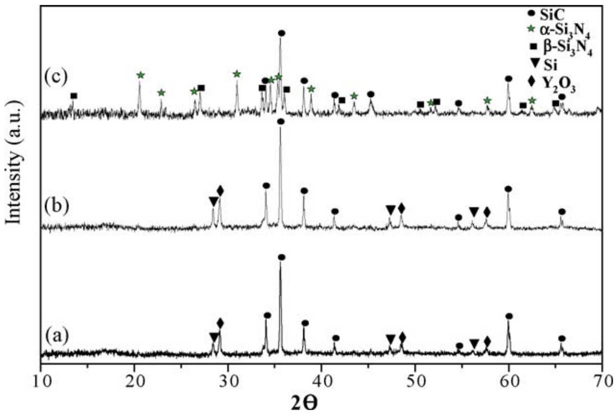


Fig. 6. XRD profiles of (a) waste SiC–5% Si powder including sintering additives; (b) after burnout and (c) after nitridation of extruded bodies.

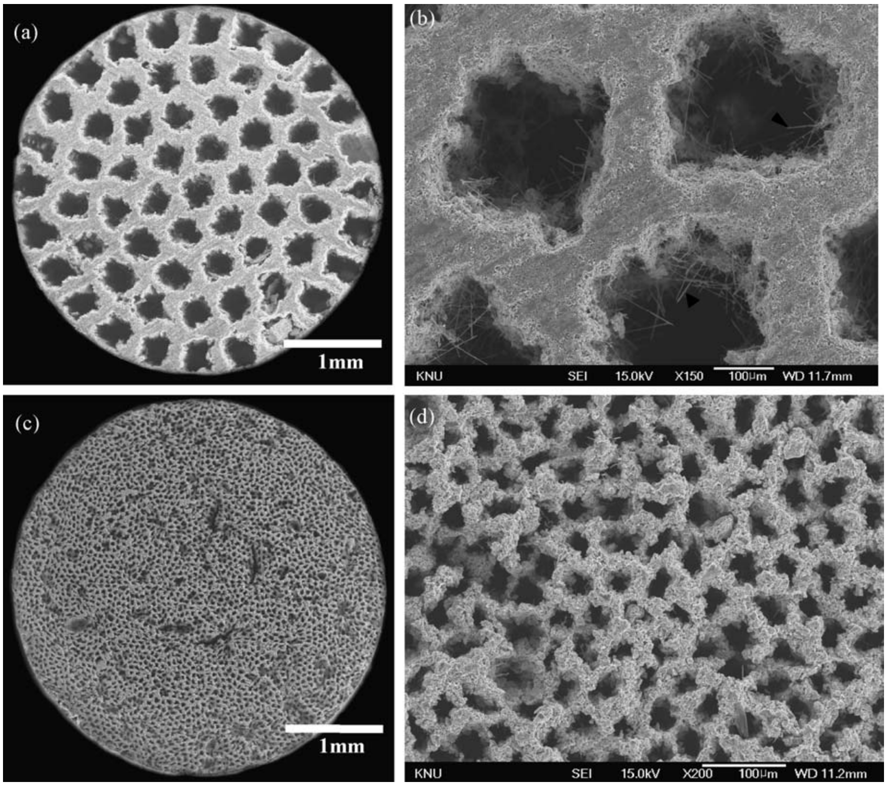


Fig. 7. SEM micrographs of porous SiC–Si_3N_4 composites after nitridation (a) second passed; (c) third passed and enlarged image of (b) the second passed and (d) third passed.

Si_3N_4 whiskers were formed by the vapour–solid (VS) mechanism by the reaction between SiO_2, C and N_2 gas during the nitridation process.[16] However, as shown in Fig. 7(b), the existence of Si_3N_4 whiskers on the continuous pore wall in the SiC–Si_3N_4 composite will have a beneficial effect on their use as filters, which function like the hairs of nostrils. The pore size of the second passed and third passed SiC–Si_3N_4 composite was 260 μm and 35 μm in diameter, respectively.

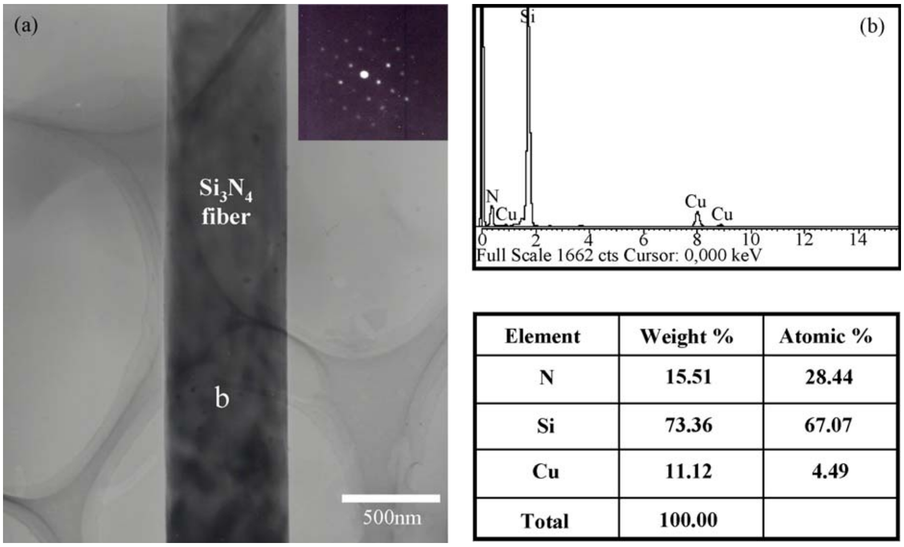
To clearly identify the Si_3N_4 whisker as shown in Fig. 7(b), TEM observation was carried out. Fig. 8(a) is a TEM micrograph and electron diffraction pattern showing the whisker morphology that was frequently observed inside the pore surface of the continuously porous SiC–Si_3N_4 composites. Most of whiskers having about 600 nm in diameter existed with in crystalline phase. From the EDS profile (b) taken in the marked ‘b’, region of Si_3N_4 whisker, it is confirmed that the whisker is Si_3N_4 phase. The detection of Cu element came from the Cu grid of TEM specimen.

Table 2 shows the material properties of continuously porous SiC–Si_3N_4 composites depending on the number of extrusion pass at room temperature. The average bending strength and hardness of the second passed samples having 57.97% in relative density were, respectively, 62.97 MPa and 388 Hv, while the third passed samples having 67.07% in relative density was 77.82 MPa and 423 Hv, respectively.

Fig. 9 shows the TEM micrograph and EDS profiles of the pore frame part in the porous SiC–Si_3N_4 composite. The EDS profiles of P, Q and R were taken from the P, Q and R region of Fig. 9(a), respectively. In Fig. 9(a), the lower right side is the thin region of the TEM sample. SiC grains were comparatively large without any internal defects. However, Si_3N_4 grains as indicated with an arrowhead were very fine less than about 100 nm in diameter because they were directly nitrided from Si particles. However, some residual pores were also observed in the frame region because the samples were just nitrided at a comparatively low temperature without post-sintering. A few Fe phases were also observed in the R region of Fig. 9(a). Near the Fe phase, some cavities were observed as indicated with an arrow and a strong strain field also was observed in the Fe phase. In general, the existence of Fe phases in the SiC–Si_3N_4 composite will have a detrimental effect on the mechanical properties.[17] Thus, in the case of

Table 2
Material properties of continuously porous SiC–Si_3N_4 composites

Properties specimens	Pore size (μm)	Bending strength (MPa)	Hardness (Hv)	Relative density (%)
Second pass sample	265	62.97	388	57.97
Third pass sample	35	77.82	423	67.07



Element	Weight %	Atomic %
N	15.51	28.44
Si	73.36	67.07
Cu	11.12	4.49
Total	100.00	

Fig. 8. TEM micrograph and electron diffraction pattern (a) and EDS profile (b) of Si_3N_4 whisker.

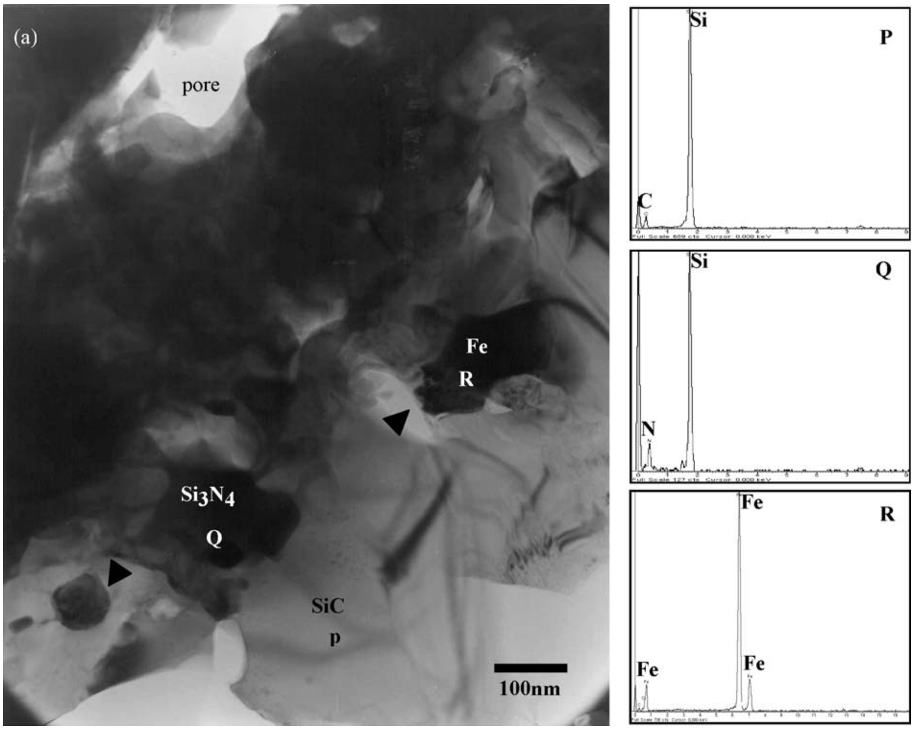


Fig. 9. TEM micrograph and EDS profiles of porous SiC–Si_3N_4 composites after nitridation.

raw SiC powder, chemical treatment is required to remove the Fe impurity.

4. Conclusions

Continuously porous SiC–Si_3N_4 composites were successfully fabricated by extrusion process using waste SiC powder. The size of pores was well controlled by an extrusion process. In the continuously porous composites, the major phases were the SiC, α-Si_3N_4 and β-Si_3N_4, but a few Fe phases were also detected as minor phases. On the wall of continuously porous SiC–Si_3N_4 bodies, many whiskers, which function like hairs of nostrils were observed with about 600 nm in diameter. The pore size of the second passed and third passed nitrided bodies was, respectively, about 260 μm and 35 μm in diameter, while the bending strength and hardness in both samples were 62.97 MPa, 388 Hv and 77.82 MPa, 423 Hv, respectively.

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