

Synthesis of porous silicon nitride using silica/carbon composite derived from phenol–resorcinol–formaldehyde gel



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ABSTRACT

Mesoporous silicon nitride (Si₃N₄), which is one of the most promising structural materials for applications in high-temperature filtration, was synthesized from the carbothermal reduction and nitridation of a pyrolyzed silica-containing phenol–resorcinol–formaldehyde (PRF) gel. The PRF gel was synthesized by combining sol–gel and polymerization of phenol, resorcinol and formaldehyde using sodium carbonate as a catalyst. Silica was incorporated into the gel by addition of 3-aminopropyl trimethoxysilane (APTMS) as a silica precursor. After aging and being freeze-dried, the silica/PRF composite was pyrolyzed under nitrogen gas to convert it into porous silica/carbon composite. The combination of phenol–formaldehyde (PF) and resorcinol–formaldehyde (RF) gels into PRF gel, allows further enhancement in porosity of the silica/carbon composite via pre-calcination in the range of 400–500 °C, since carbon derived from PF gel and that from RF gel have different thermal stability. The final product obtained after final calcination to remove residual carbon has a surface area as high as 194 m²/g, which is significantly much higher than the conventional Si₃N₄ granules. Specific surface area of the product is affected by molar ratio of phenol-to-resorcinol, molar ratio of silica-to-carbon, and the pre-calcination temperature.

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1. Introduction

Silicon nitride (Si₃N₄) is one of the most promising advanced ceramic materials. Because of its unique properties such as low density, high high-temperature strength, high stress and damage tolerance, good thermal stress resistance, and high reliability compared to other ceramics, it has been widely used in many high-temperature applications such as structural components of gas turbines, reciprocating engine parts, bearing, and cutting tools [1]. Recently, porous Si₃N₄ has attracted great interest in engineering applications because of its increased surface area together with its good high-temperature properties, which makes it a good candidate for applications like high-temperature gas filters and catalyst supports for high-temperature reactions [2]. Various techniques have been used to fabricate porous Si₃N₄ such as partial sintering, restrained sintering, partial hot-pressing, and freeze-drying, but the surface area achieved is still low or moderate [3–6]. Another approach is the synthesis via the carbothermal reduction and nitridation using porous silica/carbon composite [7]. One of the sources for producing porous carbon with large mesopore

volume is resorcinol–formaldehyde (RF) gel, which is a product from polycondensation of resorcinol and formaldehyde [8]. Silica can be conveniently introduced into the gel via the sol–gel process, while the RF gel is formed. Then, the gel can be converted into highly porous silica/carbon composite via the pyrolysis. Porosity of the composite enhances the transfer of nitrogen to the reaction sites during the carbothermal reduction and nitridation process, resulting in mesoporous Si₃N₄ or Si₃N₄/SiC composites.

Having known that phenol–formaldehyde (PF) gel can also be pyrolyzed into porous carbon aerogel in similar manner as the RF gel, the idea of combining PF gel with RF gel to form phenol–resorcinol–formaldehyde (PRF) gel has been brought into attention. Since oxidation of carbon derived from RF and PF gels occurs at different temperatures [9], calcination of the carbonized PRF gel at proper temperature might lead to a composite with enhanced porosity. This approach also offers a benefit of controlling variety of factors that influence the structure of carbon gels. Therefore, this technique is considered as a simple method to prepare porous Si₃N₄ without a special equipment or complicated procedure.

In this work, effects of various parameters, such as composition of the PRF gel, silica-to-carbon molar ratio of the composite, and calcination temperature to partially remove carbon from the silica/carbon composite are investigated. Detailed preparation procedures, characteristic of the products, and mechanism of the

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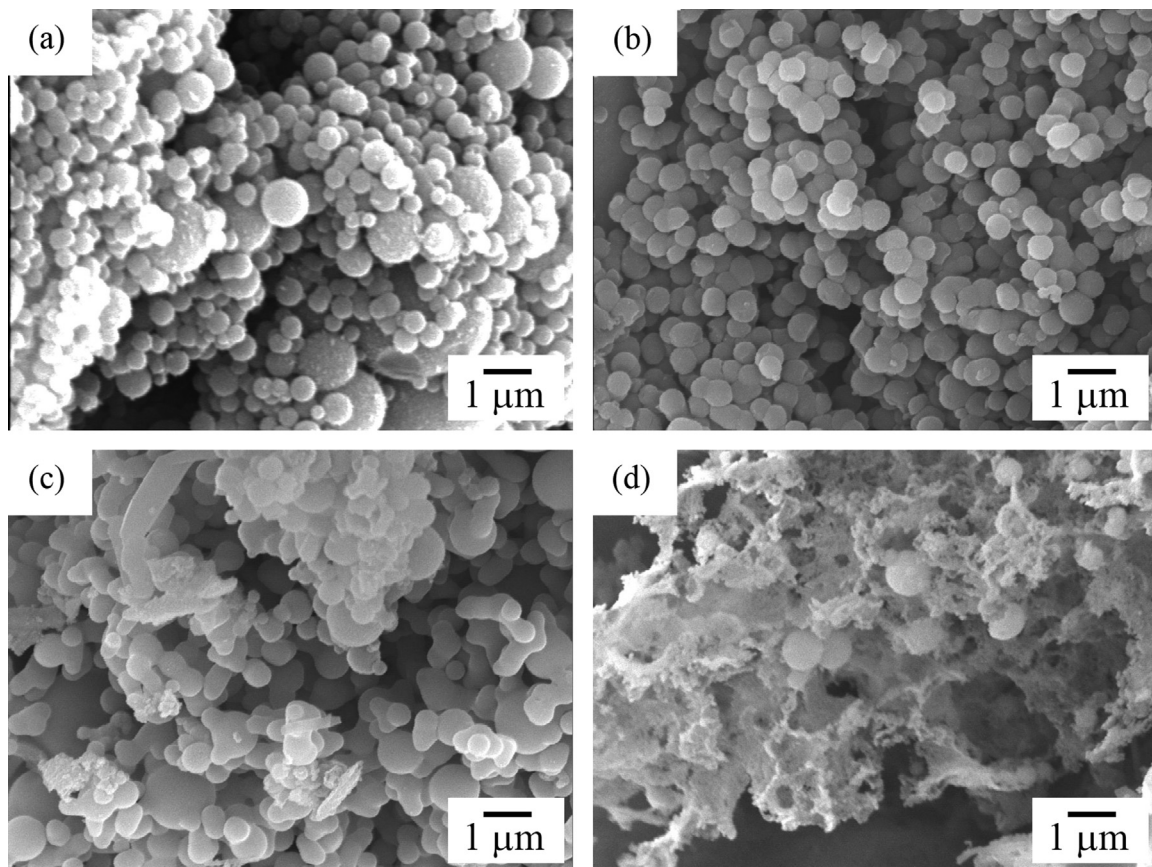


Fig. 1. SEM micrographs of silica/PRF composite prepared using P/R molar ratio of 0.5 and SiO_2/C molar ratio of 0.05: (a) after pyrolysis, (b) after pre-calcination at 450 °C, (c) after nitridation, and (d) after final calcination.

process are discussed.

2. Experimental

2.1. Preparation of silica/PRF gel

Phenol (P, 99%; Asia Pacific Specialty Chemical, Sydney, Australia) and resorcinol (R, 99.8%; Asia Pacific Specialty Chemical, Sydney, Australia) were firstly dissolved into deionized water (W) and were stirred until the dissolution was completed. For this study, the R/W molar ratio was kept at 0.5, while the P/R molar ratio was varied from 0.3–1.5. Then, sodium carbonate (C, 99.8%; Asia Pacific Specialty Chemical, Sydney, Australia), which was used as a catalyst for PRF gel formation, was added into the solution at the C/W ratio of 10 mol/dm³. The mixture was stirred at room temperature for 15 min. Next, formaldehyde solution (F, 37%; Asia Pacific Specialty Chemical, Sydney, Australia) was added, using the R/F molar ratio of 0.5. After the mixture was stirred for 15 min, 3-aminopropyl trimethoxysilane (APTMS, 97%; Sigma-Aldrich, Milwaukee, WI) in the predetermined amount was added to the solution under continuous stirring. The mixture was aged at room temperature without stirring for 3 days. After aging, solvent in the gel was removed by solvent exchange process, i.e. the sample was immersed in *t*-butanol for 3 days, renewed with fresh *t*-butanol every day. Finally, the gel was removed from *t*-butanol and was dried using freeze drying process at –40 °C for 3 days to obtain silica/PRF gel.

2.2. Preparation of silica/carbon composite

Porous silica/carbon composite was obtained by pyrolysis of the dried silica/PRF gel in step-wised fashion. The dried gel was heated under continuous flow of nitrogen gas (25 ml/min) in a tubular flow reactor operated at 250 °C for 2 h and subsequently heated up to 750 °C and held at that temperature for another 4 h. The heating rate employed was 10 °C/min. Finally, the sample was pre-calcined in a box furnace at the controlled calcination temperature in the range of 400–500 °C for 2 h to partially remove carbon from the composite. The product obtained in this step is porous silica/carbon composite.

2.3. Synthesis of porous silicon nitride

In the carbothermal reduction and nitridation process, the silica/carbon composite was put into an alumina tray (25 mm × 15 mm × 5 mm deep) and placed in a horizontal tubular flow reactor. The composite was then heated to 1450 °C using a heating rate of 10 °C/min under a continuous flow of argon (50 l/h). After the temperature had reached the set-point, the supplied gas stream was switched from argon to a mixture of 90% nitrogen and 10% hydrogen with the same total flow rate to initiate the reaction. The reaction was held at constant temperature for 10 h. The obtained product was subsequently calcined in a box furnace at 800 °C for 8 h to remove residual carbon.

2.4. Products characterizations

Microstructure and morphology of grains in the samples were investigated by scanning electron microscopy (SEM, Jeol JSM-

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