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Original Article

Synthesis, characterization and sintering of Si-C-N nano-powders via sodium reduction in liquid ammonia

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ABSTRACT

Si-C-N nano-powders with tunable carbon content were synthesized through the reduction of silicon tetrachloride (SiCl_4) and trichloromethylsilane (SiCl_3CH_3) solution by sodium in liquid ammonia. The nano-powders contain two domains of structure, Si-C-N amorphous or continuous random networks (CRNs), and free carbon. The carbon content in $\text{Si}_{3+n}\text{C}_n\text{N}_4$ CRNs, is tunable from $n = 0$ to $n = 1$. Free carbon will appear with the increase of the C/Si mole ratio when C/Si is higher than 1/4. The crystallization of amorphous Si-C-N powders occurs at temperatures ranging from 1300 °C to 1500 °C depending on the carbon content. The additive-free dense Si-C-N ceramics with relatively low porosity were fabricated by Spark Plasma Sintering (SPS).

1. Introduction

Ceramics based on silicon nitride and silicon carbide are finding increasing application due to their unique properties such as low density, high thermal conductivity, high-temperature stability, low dielectric constant and high resistance to chemical attack because of their potential of high strength and toughness. [1] However, preparing fully dense and stoichiometric Si_3N_4 -SiC ceramics is still a challenge. [2,3] In recent years, polymers like polysilazanes have been developed to improve the homogeneity of the microstructure of the SiC- Si_3N_4 composites without addition of metal oxides. [4–7] However, two factors make it impossible to prepare large and dense Si-C-N samples. One factor is associated with the outgassing of hydrogen and hydrocarbons during the polymer to ceramic transformation, [6] and another factor is that the non-stoichiometric Si-C-N matrix decomposes and partitions by the loss of nitrogen [8] This group of ceramics of the general composition of $\text{Si}_{3+x}\text{C}_x\text{N}_4$, remains stable below 1425 °C and gives off nitrogen when the temperature is higher than 1425 °C as long as the system reaches the tie line composition of $\text{Si}_{3+x}\text{C}_x\text{N}_4$. The synthesis routes that allow the direct formation of $\text{Si}_{3+x}\text{C}_x\text{N}_4$ compositions by the polymer to ceramic transformation is still a hot area of research. [9] Conventionally, carbon content is tuned by reactive heat treatment of polymer derived materials with different atmosphere, [10] but this process is complicated. It was reported that the polymer derived Si-C-N composite usually contains two nano-domains: continuous random

networks(CRNs) and free carbon. [7,8]

Our group provides a novel method to synthesize nano-sized amorphous nitride powders and dense ceramic bulks through the reduction of silicon tetrachloride (SiCl_4) by sodium in liquid ammonia successfully. [11] The Si_3N_4 nano-powders obtained through this method is in amorphous structure. Therefore, in present work, we report the possibility of introducing carbon atoms into Si-C-N amorphous network directly through the same reduction method and analyze the structure of the Si-C-N nano-powders.

2. Experiment

The synthesis reaction was carried out in liquid ammonia. The experimental process is similar to our previous work. [11–13] SiCl_4 (Alfa Aesar, 99.998%) was used as the raw materials for silicon source. CCl_4 and SiCl_3CH_3 (Aladdin, 99%,) were used as the carbon source respectively. SiCl_4 was mixed with SiCl_3CH_3 first. Because SiCl_4 and SiCl_3CH_3 could dissolve with each other in the entail composition, the composition of silicon can be easily adjusted with carbon in the raw material solution. The proportion of SiCl_4 and SiCl_3CH_3 in the mixture solution is shown in Table 1. The samples were labeled based on the molar ratio of Si and C in the raw materials, e.g. solution with the SiCl_4 and SiCl_3CH_3 mole ratio of 9:1, 3:1, 2:1 and 0:1, were labeled as, S10-1, S4-1, S3-1, and S1-1, respectively. The reaction was adopted by slowly dripping the raw material solution into the solution of sodium (2% excess) in

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Table 1
Chemical composition of raw material solution.

Sample	(SiCl ₄ : SiCl ₃ CH ₃)	x _{Si} : x _C
S10-1	9:1	10:1
S5-1	4:1	5:1
S4-1	3:1	4:1
S3-1	2:1	3:1
S5-3	2:3	5:3
S1-1	0:1	1:1

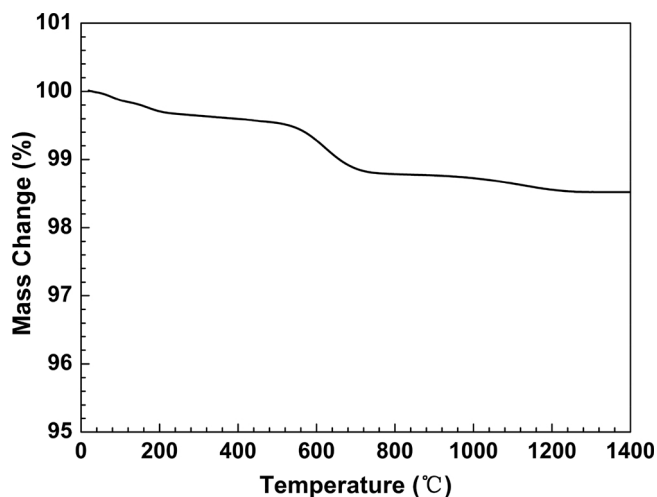


Fig. 1. Thermal gravimetric analysis (TGA) of the sample S4-1 in flowing Ar, heating rate: 300 °C/h.

Table 2
Chemical Composition of product powders (at %).

Sample	Si	C	N	Phase Composition
S10-1	43.4	4.2	52.4	Si ₃ N ₄ + 0.31SiC
S5-1	44.0	8.2	47.8	Si ₃ N ₄ + 0.68SiC
S4-1	44.6	10.4	45.0	Si ₃ N ₄ + 0.96SiC
S3-1	43.7	12.2	44.1	Si ₃ N ₄ + SiC + 0.14C
S5-3	41.8	16.7	41.5	Si ₃ N ₄ + SiC + 0.58C
S1-1	38.8	23.0	38.2	Si ₃ N ₄ + SiC + 1.35C

ammonia. The product powders were extracted by Soxhlet extraction method with liquid ammonia to remove the by-product NaCl. Heat treatment was carried out at 600 °C to 1500 °C in corundum crucible in Ar atmosphere. Only small amount of NaCl residues, 0.4 wt% and 0.1 wt%, remained in the product powders after 100 cycles extraction, and in the product powders after heat treatment at 900 °C.

The composition of the obtained powders was measured using different methods. The silicon and impurity sodium content were measured by means of ICP-AES (Shimadzu AA 6800), nitrogen and oxygen content was quantified by an O/N analyzer (Leco TC-436), and carbon element was measured by a C/S analyzer (ELTRA CS 800), chlorine elements were detected by Mohr's titration method.

To get the ceramic bulks, the synthesized Si-C-N powders were sintered by spark plasma sintering (SPS) (Dr. Sinter 1050 spark plasma sintering system, Sumitomo Coal Mining Co., Tokyo, Japan.) at 1550 °C with the pressure of 50 MPa for 5 min in vacuum. The heating rate was 100 °C per minute, and rapid cooling was performed by turning off the power of the furnace (cooling rate: > 200 °C/min, above 900 °C).

The product powders were first characterized by X-ray diffraction (XRD Rigaku, D/max-RB) analysis. The structural evolution of the free

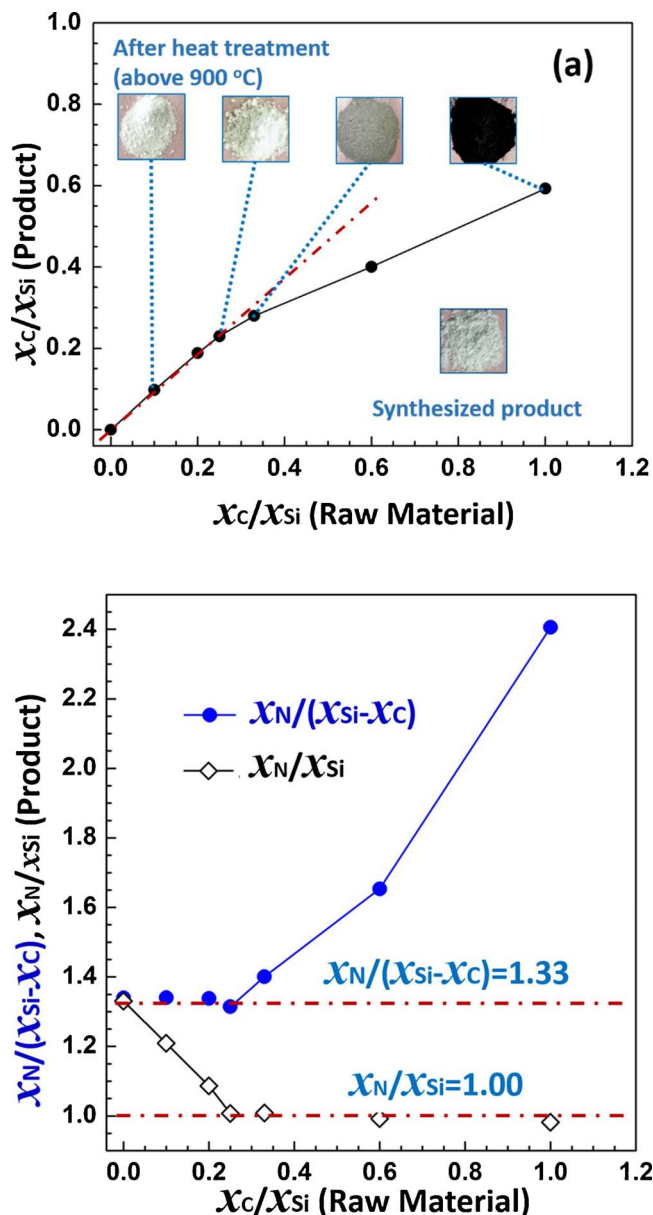


Fig. 2. Composition of carbon (a), nitrogen (b) in the product as the function of x_C/x_{Si} ratio in the raw material.

carbon phase was characterized by high-resolution Raman spectroscopic analysis (Horiba-labram HR evolution) with excitation at 532 nm. The chemical environment around the Si, C, and N atoms in the materials was investigated by X-ray photoelectron spectroscopy (XPS, Kratos, Axis Ultra DLD). The morphologies of the samples were observed through transmission electron microscope (TEM, JEOL, JSM-2010) through which the high-resolution electron microscopy (HREM) could be studied. The morphologies of the ceramic sintered by Spark Plasma Sintering (SPS) were observed through field emission scanning electron microscopy (FESEM, JEOL, JSM-6701F).

3. Results and discussion

Carbon was not detected in the solid products when CCl₄ was used as carbon source in raw material for the reaction with Na-NH₃ solution, while CH₄ was detected in the outlet gas phase. The reaction of CCl₄

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