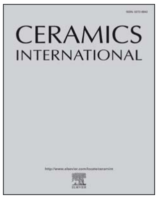
Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Effect of SNNWS content on the microstructure and properties of SNNWS/Si-C-N ceramic composites via PIP

Yuanyi Zheng[1], Duan Li[1], Bin Li*, Shitao Gao, Xuejin Yang

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, China

ARTICLE INFO

Keywords:
Si_3N_4 nanowire
SiCN ceramic
Precursor infiltration and pyrolysis (PIP)
Composites
Mechanical properties
Thermophysical properties

ABSTRACT

Si-C-N ceramic composites containing well distributed silicon nitride nanowires (SNNWs) were fabricated by die-pressing and precursor infiltration and pyrolysis process at a low temperature. The structure, composition, mechanical and thermophysical properties of the composites were investigated. The results show that the composites consisted of amorphous SiCN, α-Si_3N_4 and α-cristobaslite. The composites with different contents of SNNWs possessed a density of 2.02–2.07 g cm^{-3} and open porosity of 7.9–9.9%. SNNWs can effectively restrain the contraction of matrix with a decrease by 25% in linear shrinkage. The composites with 3 wt% SNNWs owned the highest flexural strength (83.7 MPa) and elastic modulus (54.0 GPa) at room temperature, which increase by 13.2% and 62.3% respectively, compared with pure SiCN ceramics. The SNNWs displayed good reinforcement function at high temperature due to the fact that the composites with 7 wt% SNNWs had a 96.8% retention rate of bending strength at 1200 °C. The composites had relatively low coefficient of thermal expansion and thermal diffusivity which were less than $2.2 \times 10^{-6}\ K^{-1}$ and 0.62 $mm^2\ s^{-1}$, respectively.

1. Introduction

Si_3N_4 nanowires (SNNWs) have received increasing attentions due to their outstanding properties such as high mechanical strength [1], variable band gaps [2,3], and low cost [4]. The large aspect ratio and small size provide SNNWs superior properties than their corresponding bulk materials. Zhu et al. [5] observed a reversible bending phenomenon of SNNWs under an illumination of electron beam. Jing et al. [6] measured the bending modulus of single Si_3N_4 nanobelt which was up to 570 GPa. It has also been proved that SNNWs can be a good candidate as the reinforcement in composites, especially the ceramic matrix composites (CMCs). Wang et al. [7,8] in-situ fabricated the SNNWs on carbon fiber fabrics and then densified the fabrics using chemical vapor infiltration (CVI) technique to form mini-C/SiC composites reinforced by SNNWs. The resulted matrix strength and fracture strength of the composites were ~100% and 8% larger, respectively, and the duration of CVI cycles was 50% shorter than that without SNNWs. Polymer derived SiCN ceramics exhibit excellent high-temperature stability, oxidation resistance, creep resistance and considerable mechanical properties due to their three-dimensional covalent Si–C–N network [9]. Introducing the SNNWs in SiCN may improve its mechanical properties, promoting the application in aero-engine materials.

The performance of composites reinforced by 1D nanostructures depends on the dispersion behavior, which can be influenced by the aspect ratio of 1D nanostructures [10–12]. To homogeneously disperse SNNWs is always difficult as they have a high aspect ratio and are prone to tangle together. The introduction of nanowires into CMCs by in-situ synthesis can be an improvement and has been reported [13–17]. However, there are still several problems. One is that the temperature for in-situ preparation of SNNWs growing on the fibers is always higher than 1300 °C [18–21] which would degenerate the properties of fibers. Moreover, to precisely control the SNNWs content by in-situ method is difficult. Besides, in-situ synthesis cannot guarantee the uniform dispersion of SNNWs as they tend to grow around the surface area rather than inner area [7,8]. To our best knowledge, there is no ideal method for dispersion of SNNWs in the composites so far.

The precursor infiltration and pyrolysis (PIP) route could be a promising method to fabricate shaped non-oxide CMCs [22]. The main advantages of PIP route involve low firing temperature, high purity, and homogeneous ceramic matrices, as well as its wide applications in making complex and near net shaped parts [23,24]. Thus, it is a promising way for preparing SNNWs/SiCN composites via PIP route.

In this work, the SNNWs were dispersed into Si-C-N matrix though high-speed shearing. Then, the powder mixture was sieved and molded by die-pressing. Afterwards, the green-bodies were pyrolyzed and then densified by PIP process. The composition and microstructures of the

---

* Corresponding author.
E-mail address: libin@nudt.edu.cn (B. Li).

[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.ceramint.2017.12.110
Received 26 October 2017; Received in revised form 29 November 2017; Accepted 15 December 2017
0272-8842/

Please cite this article as: Zheng, Y., Ceramics International (2017), https://doi.org/10.1016/j.ceramint.2017.12.110

composites were characterized and the effects of SNNWs on the density, mechanical and thermophysical properties were analyzed.

2. Experimental procedure

2.1. Materials and processing

The polysilazane PSZ-50 (Eisen new material technology co. LTD, Hangzhou, China) with a mole ratio of Si:C:N = 1:1.13:2 was used in present work (see the molecular structure in formula (1)). The method to synthesize SNNWs was reported in previous work [19]. Synthesis of porous SNNWs/SiCN skeleton took place as following steps. Firstly, curing of polysilazane was carried out by heating it to 220 °C slowly in air and held for 10 h. Afterwards, the temperature was increased to 250 °C with another dwell time of 10 h and then the partially cured polysilazane was obtained. Secondly, the cured polysilazane was ground to powder by pulverizer (FW-80, Yongguangming medical instrument co. LTD, Beijing) and mixed with SNNWs by pulverizer followed by sieving with 350 μm mesh. Thirdly, the sieved powder mixture was cold pressed into green bodies with a dimension of 40 mm × 35 mm × 5 mm at 100 MPa in the single injection hydraulic press. Subsequently, the green bodies were pyrolyzed in nitrogen flow at atmospheric pressure. The furnace was heated to 300 °C at a rate of 3 °C min^{-1} and then kept for 1 h for further crosslinking and curing. Finally, the furnace was heated to 1300 °C for 2 h at a rate of 5 °C min^{-1} and the porous ceramic skeleton was acquired after cooling. 1300 °C is quite proper because that SiCN prepared at lower temperatures exhibited worse high-temperature oxidation resistance and the three-dimensional covalent Si–C–N network will be broken at higher pyrolysis temperatures (> 1400 °C).

$$-[Si(CH_3)CH = CH - NH - Si(CH_3)H - NH]_n- \qquad (1)$$

PIP process was employed for densifying the SNNWs/SiCN skeleton. First of all, the polysilazane was dissolved in hexane and the skeleton was fully immersed in the solution for 2 h under vacuum. After that, the skeleton was dried at ~70 °C in a vacuum oven. Finally, the curing and pyrolysis process were applied and the procedure was the same as mentioned above. SNNWs/SiCN composites with varying SNNWs contents (0, 1.0 wt%, 3.0 wt%, 5.0 wt% and 7.0 wt%) were obtained by repeating the PIP process for 5–7 times. Fig. 1 depicts a schematic diagram for the process of fabricating SNNWs/SiCN composites.

2.2. Characterization

Density and open porosity of the ceramic composites were measured by Archimedes' method in distilled water at 20 °C. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) and X-ray diffractometer (XRD, D8 Advance, Bruker/Axs Corp., Germany) were employed to analyze the structure and phase composition. The microstructures were observed on a Hitachi S-4800 scanning electron microscope (SEM). The flexural strength and elastic modulus were tested via a three-point bending test machine (WDW-100, Changchun Research Institute of Test Machines, Jilin, China) with a support distance of 20 mm and a loading speed of 0.5 mm min^{-1} at room temperature. Five rectangular specimens with a dimension of 25 mm × 3 mm × 2.5 mm were tested to obtain an average strength. The high-temperature mechanical properties were tested by the same way with a heating rate of 10 °C min^{-1} and a hold time of 5 min for each temperature. The fracture toughness (K_{IC}) was measured using single edge notched beam (SENB) method with a span of 20 mm and a loading speed of 0.05 mm min^{-1} at room temperature. At least five specimens with a dimension of approximately 25 mm × 2.5 mm × 5 mm and a 2.5 mm thick edge notch were tested to obtain the average toughness. The coefficient of thermal expansion (CTE) was tested by a thermal dilatometer (DIL 402 C, NETZSCH Corp., Germany) with a heating rate of 5 °C min^{-1} and the dimension of the test piece was 25 mm × 5 mm × 5 mm. The thermal diffusivity was measured using a laser thermal conductivity testing instrument (LFA 447, NETZSCH Corp., Germany) with a dimension of Φ12.7 mm × (2 − 4) mm.

3. Results and discussion

3.1. Structure, composition and morphology

Fig. 2 shows the morphology of the as-received SNNWs and the SNNWs/PSZ powder mixture after sufficient dispersion. It can be seen that the SNNWs possess a length of several hundred micrometers (Fig. 2a) and a diameter of 100–300 nm (Fig. 2b). A homogeneous

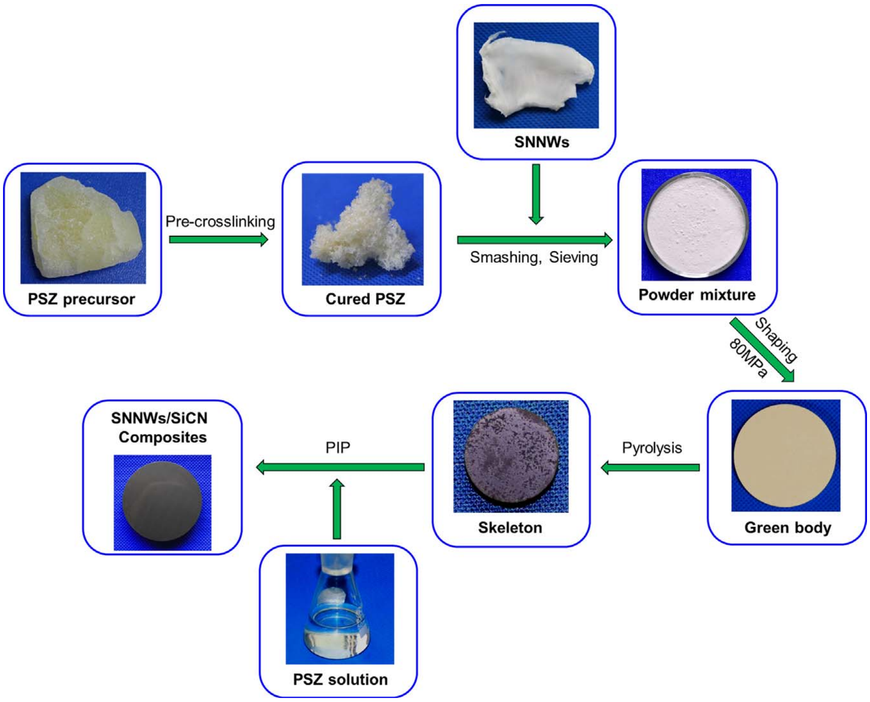


Fig. 1. Schematic diagram for the preparation of SNNWs/SiCN composites.