Ceramics International 43 (2017) 6110–6116

Contents lists available at ScienceDirect

Ceramics International

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

Effect of temperature and gaseous medium on the evolved microstructures of carbon fiber reinforced reaction bonded silicon nitride composites

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ARTICLE INFO

Keywords:
B. Composite
B. Whiskers
D. Si_3N_4
Reaction bonding

ABSTRACT

Reaction bonded silicon nitride (RBSN) composites containing 10 vol% carbon fiber were prepared using the direct nitridation method at 1200, 1300 or 1400 °C by purging pure nitrogen or nitrogen-hydrogen (95% N_2-5% H_2) mixed gas. The effect of nitridation temperature and gaseous medium on the microstructure of RBSN were studied in detail. X-ray diffraction analysis on the resultant RBSN composites revealed a dominant α-Si_3N_4 phase along with β-Si_3N_4 and Si_2N_2O. The growth of silicon nitride whiskers was found to increase with the addition of carbon fibers. The microstructural analysis using TEM and SEM ascertained that there was no formation of beads at the tip of the whiskers. Hence, the growth of whiskers purely depends on gas phase reactions, i.e., it is based on vapor-solid (VS) and not vapor-liquid-solid (VLS) mechanism.

1. Introduction

Silicon nitride is one of the best non-oxide ceramic materials for structural applications. It has good high-temperature strength, high corrosion resistance, good oxidation resistance, better thermal shock resistance, low thermal expansion and high thermal conductivity [1]. Silicon nitride ceramics can be made by many methods, like hot pressing (HP) or hot isostatic pressing (HIP), pressureless sintering (PS), gas pressure sintering (GPS), spark plasma sintering (SPS) of silicon nitride powder and reaction bonding (RB) of silicon powder/compact under nitrogen atmosphere [2–6]. Each method has its own advantages and disadvantages. It is difficult to sinter the silicon nitride due to the highly covalent nature. Many liquid phase forming oxide additives have been used for achieving good density [7]. However, the oxide phase is detrimental to the high-temperature properties of silicon nitride. Reaction bonded silicon nitride (RBSN) ceramics can be made by direct nitridation of silicon powder/compact at a temperature range close to the melting point of silicon, i.e. in the temperature range of 1200–1450 °C. RBSN ceramics have many advantages, such as low cost of raw materials, low cost of production, easy control of dimensions and very less or no machining required for post processing. On the negative side, they are left with 15–20% porosity and unreacted silicon [8]. To achieve high density, RBSN ceramics can be post-sintered using different sintering techniques. Very less machining is required for sintered RBSN than the sintered silicon nitride (SSN) [9]. In order to get better density and to avoid post-sintering, pre-sintering of silicon is carried out to the desired level of green density prior to nitridation [10]. Dense silicon nitride ceramics are used for turbine blades, turbochargers, rotors, heat exchanger and ball bearings, while the porous silicon nitride ceramics are used for molten metal filters, catalyst carriers and radomes [8,11]. The effective nitridation rate controlling parameters are temperature of nitridation [12], particle size and surface area of silicon powder [13], impurities present in the silicon powder [14,15], gaseous atmosphere (N_2, N_2+H_2, NH_3) used during nitridation [16–18], nature of gas flow (static or dynamic) and the duration of nitridation [19,20]. Many methods are available for making silicon powder preform for the reaction bonding process, like slip casting [21], gel casting [22] and die pressing [6].

In this work, an attempt has been made to prepare the carbon fiber reinforced silicon nitride composites by RB method. The effect of processing parameters (temperature and gaseous medium) and carbon fiber on the evolved microstructure of RBSN composites has been studied. Nitridation reaction mechanisms are discussed in details.

2. Materials and methods

2.1. Starting materials

Silicon powder and short carbon fibers were used as the starting materials to prepare the carbon fiber reinforced reaction bonded silicon nitride composites. The as-received silicon powder has average particle size of 9 μm (Metal powder company Ltd., Tamilnadu, India). The chopped carbon fibers are 6 mm in length and 7 μm in diameter (Jalark carbon products, Gujarat, India).

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http://dx.doi.org/10.1016/j.ceramint.2017.02.004
Received 22 September 2016; Received in revised form 29 January 2017; Accepted 1 February 2017
Available online 02 February 2017

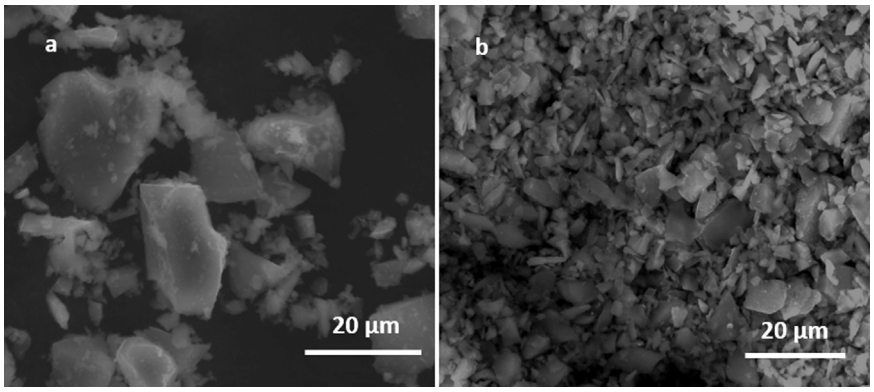

Fig. 1. SEM micrographs of silicon powder: (a) as received and (b) ball milled for 12 h.

2.2. Methods

The as-received silicon powder was wet milled for 10 h using tungsten carbide milling media in high energy planetary ball mill in order to get more surface area by reducing the particle size. This is mainly to enhance nitridation reaction. Ethanol was used as the process controlling medium. The chopped carbon fibers (10 vol%) were ultrasonically dispersed in ethanol for 15 min. The pre-dispersed fibers were mixed with the silicon powder slurry and further milled for 2 h to get a homogeneous dispersion. After the ball milling, the mixed slurry was mechanically agitated using a stirrer to improve the dispersion. The mixture was then dried and stored in a vacuum desiccator till further processing. The appropriate quantity of dried powder was mixed with 2 wt% polyvinyl alcohol (PVA) binder using a mortar and pestle. The mixture was compacted at 250 MPa pressure. Silicon powder compacts without carbon fiber were also made for comparison purpose. The mass of the green compacts was determined and then loaded in an alumina boat. The alumina boat was then placed at the center of the alumina tubular furnace. To optimize the temperature and gaseous medium for effective nitridation, experiments were carried out at 1200, 1300 or 1400 °C by purging pure N_2 gas or 95% N_2-5% H_2 gas for 4 h. For mixed gas nitrided samples, the samples were pre-treated by purging argon-hydrogen (95% Ar-5% H_2) gas mixture till it reaches 1200 °C and then the gas flow was switched to nitrogen-hydrogen (95% N_2-5% H_2) gas mixture. A stepwise nitridation was used for the samples nitrided at 1400 °C, i.e., the samples were soaked for 1 h each at 1200 °C and 1300 °C and then 4 h at 1400 °C. In all the above cases, the heating rate for nitridation was 5 °C/min and gas flow rate was 1 l/min.

2.3. Characterization

The particle size distribution of the silicon powder (before and after milling) was determined using Microtrac laser particle size analyzer and the surface area analysis was carried out using a BET analyzer (Smart Instruments Co., India) based on nitrogen gas adsorption. The phases present in the final products were determined by PANalytical X-ray diffractometer (XRD) with Cu K_α radiation. The microstructure and composition of the final products were analyzed using scanning electron microscope (FEI Quanta 400 and Inspect F) equipped with energy dispersive X-ray spectroscopy (EDS). The microstructure of the composites was also studied using transmission electron microscope (TECNAI 200).

Table 1
The particle size distribution and surface area of silicon powder.

Sample condition	Particle size distribution (µm)			BET surface area (m^2/g)
	d_{10}	d_{50}	d_{90}	
As received	2.2	8.7	20.4	1.6
12 h ball milled	0.1	0.2	0.9	18.3

3. Results and discussion

The SEM micrograph of as-received silicon powder (Fig. 1(a)) shows that the particles are having irregular shape. It can be seen that the silicon powder has a wide particle size distribution, which is further confirmed from the particle size analysis (Table 1). The Fig. 1(b) shows that the particle size is reduced significantly after 12 h ball milling. Some larger particles are also visible in the micrograph, however, they are not more than a few microns. The reduction in particle size can increase the surface area of the silicon powder, which will increase the nucleation sites for nitridation.

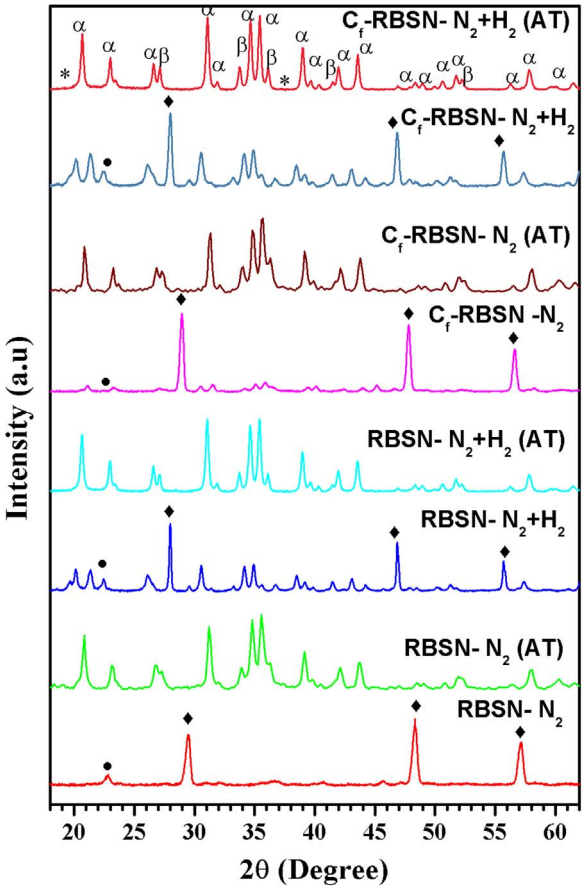

Fig. 2. XRD patterns of samples nitrided at 1200 °C using N_2 and N_2-H_2 mixture for 4 h. (*- Si_2N_2O, ♦ - Si, • - SiO_2).