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ScienceDirect

Ceramics International 41 (2015) 4326–4333

CERAMICS INTERNATIONAL

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Microwave-plasma synthesis of nano-sized silicon carbide at atmospheric pressure

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Received 11 September 2014; received in revised form 24 November 2014; accepted 24 November 2014
Available online 29 November 2014

Abstract

A microwave plasma process operating at atmospheric pressure was developed for the synthesis of SiC nanoparticles. The process utilizes methyltrichlorosilane (MTS) as precursor, acting as both carbon and silicon source, along with an additional hydrogen feed to ensure a fully reducing reaction environment. In addition, argon served as carrier gas. The parameters studied were the H_2:MTS molar ratio and the total enthalpy, in the range 0–10 and 70–220 MJ/kg respectively. The particles size distribution ranged from 15 to 140 nm as determined by SEM and TEM micrographs. It was found that an increase in enthalpy and a higher H_2:MTS ratio resulted in smaller SiC particle sizes. The adhesion of particles was a common occurrence during the process, resulting in larger agglomerate sizes.

Keywords: Silicon carbide; Microwave plasma; Nanoparticles; Methyltrichlorosilane

1. Introduction

The favourable physical and mechanical properties of silicon carbide (SiC) allow for various applications across many areas, for example, in high power and high frequency electronics as well as high temperature technologies [1,2]. At present the material is receiving increased attention as a nuclear ceramic due to its excellent mechanical properties, low neutron absorption cross-section (25% that of zirconium based alloys) and dimensional stability under irradiation [3]. Although conventional carbide ceramics exhibit certain drawbacks, such as low ductility and high brittleness, nano-sized carbide powders can easily overcome these shortcomings.

SiC nanoparticles have been shown to exhibit properties that differ substantially from that of the bulk material, encouraging the creation of new areas of application. Many different manufacturing methods for the creation of SiC nanoparticles have been reported in the literature. These include carbothermic reduction [4], pulsed laser deposition [5], sol-gel processes [6], microwave heating [7,8] as well as different plasma techniques such as inductive radio-frequency (RF) [9–11], direct current (DC) thermal [12], low pressure microwave plasmas [13] and microwave plasma assisted chemical vapour deposition [14,15]. Vennekamp et al. [16] described the formation of a SiC nanopowder using an atmospheric microwave plasma with tetramethylsilane (TMS) as precursor. They also produced growth-rate equations using the concept of Ostwald ripening, showing the dependency of particle growth rate on temperature and pressure. Microwave plasmas have also been used for the synthesis of other nanoscale substances such as Si [17], MoS_2 and WS_2 [18], WO_3 [19] and Zn and ZnO [20].

It is well known that, given the right conditions, methyltrichlorosilane (CH_3SiCl_3 or MTS) decomposes to form SiC and hydrogen chloride (HCl) shown in Eq. (1).

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http://dx.doi.org/10.1016/j.ceramint.2014.11.121
0272-8842/

$$CH_3SiCl_3 \rightarrow SiC + 3HCl \quad (1)$$

The reaction kinetics and mechanisms of this reaction have been thoroughly reported in the literature through chemical vapour deposition [21–24], chemical vapour infiltration [25], radio frequency induction plasma [26] and pyrolysis [27] investigations. In this article the synthesis of SiC nanoparticles from MTS is reported using a microwave-induced plasma, operating at atmospheric pressure in an argon/hydrogen environment. Operation at atmospheric pressure allows for the possible development of low cost, less energy intensive synthesis methods and smaller equipment footprints. MTS was used as feed material due to the benefit of having a stoichiometric silicon-to-carbon elemental ratio, and the relative ease of the procedure through which MTS can be fed into the system due to its liquid state and high vapour pressure at standard conditions. Hydrogen was fed into the reactor along with the MTS as a reductant to drive the conversion reaction. The process parameters studied were the H_2:MTS molar ratio and the total enthalpy. Argon served as the carrier gas for MTS.

2. Experimental

2.1. Apparatus

A commercial microwave source from Electronic GmbH & Co., Germany, model PGEN2450/1.5–1.5KW2AIW, was used. The equipment consists of a 1500 W power supply with a MOS-FET amplifier, a microwave generator operating at 2.45 GHz, a water-cooled magnetron head, a stub tuner, a rectangular waveguide and a sliding short. The quartz tube, in which the plasma is generated and maintained, was positioned through the middle- and perpendicular to the waveguide before the stub tuner. The quartz tube has an internal diameter of 2 cm and a length of 30 cm. An in- and outlet at the top and bottom of the quartz tube allows for the flow of gas through the plasma. The tube was cooled by blowing air into an inlet into the waveguide perpendicular to the quartz tube and letting the air pass over the tube, exiting through the top and bottom openings in the waveguide. Argon and hydrogen flow rates were controlled using Aalborg rotameters. The physical layout of the reactor assembly is illustrated in Fig. 1 and a schematic representation of the flow path is shown in Fig. 2.

MTS vapour was fed into the reactor by vapourising MTS into a bypass argon stream and passing the MTS laden argon into a cross joint where it was mixed with the main argon stream and the hydrogen feed. The total gaseous feed mixture was passed through a 0.2 μm sintered metal filter to ensure that no solid materials enter the plasma reactor and that the total gas mixture is homogenously mixed. The mass flow of MTS was controlled by varying the bubbling rate of the argon carrier. The MTS mass transfer as a function of argon flow rate in standard cubic centimetres per minute (sccm) is shown in Fig. 3. The calibration curve was determined by bubbling argon through the liquid MTS at different flow rates for 10 min each, and measuring the mass difference after each run.

The MTS vapourisation assembly consisted of a 250 mL borosilicate glass jar equipped with a lid containing an inlet and outlet port. The argon inlet line was placed below the level of the MTS. The inlet line was left open and the argon allowed to bubble freely.

Some physical properties of MTS are given in Table 1 [28].

The exit gas from the reactor was passed through a coiled 1/4" copper thermophoresis tube, cooled by immersing the tube in an ice bath, to collect any product particles, then

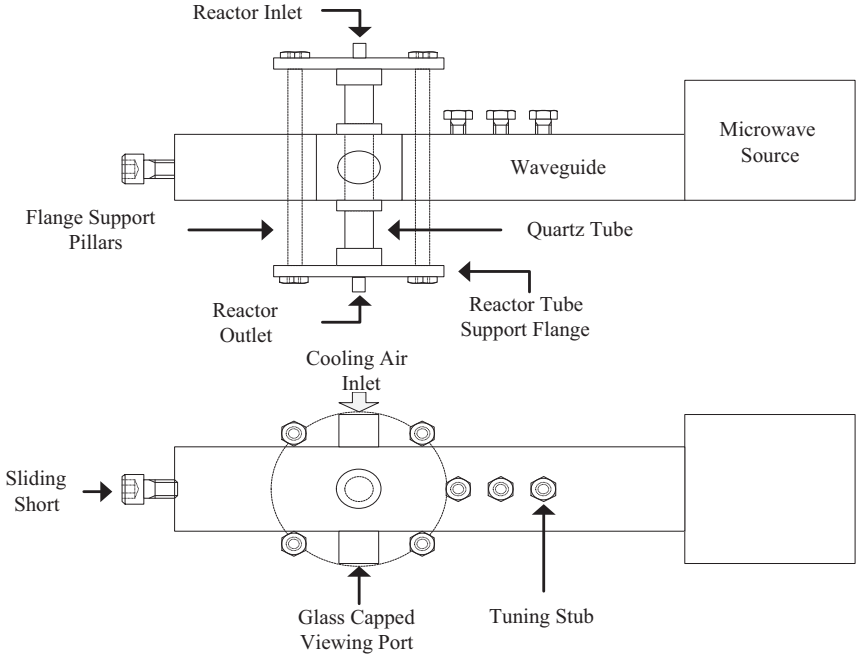

Fig. 1. Physical layout of the reactor assembly.