Induction plasma synthesis of ultrafine SiC

François Gitzhofer

Plasma Technology Research Center (CRTP), Department of Chemical Engineering
University of Sherbrooke, Québec, J1K 2R1, CANADA.

Abstract: Induction plasma synthesis of ultrafine powders has been studied using different precursors, different plasma torch configurations and injection conditions. The long residence time available in the r.f. plasma, as well as the high temperature are necessary conditions for decomposition in the vapor phase of the injected species. High cooling rates of the plasma gas in the condensation region of the reactor guarantees homogeneous nucleation of SiC or doped SiC with limited heterogeneous nucleation by the reactor wall. Heat and mass transfer in the r.f. induction plasma have been intensively studied both experimentally and theoretically with the developement of reliable numerical models. The synthesis of SiC in the induction plasma can benefit from these data to design the reactors. Many parametric studies have shown that it is possible to influence and maintain SiC UFP quality. Solid elemental Si as a starting material is a promising avenue for UFP SiC synthesis.

INTRODUCTION

The term "ultrafine powders" (UFP), also called nanosized powders, refers to particles sized between 5 and 100nm. The demand for advanced ceramic powders (including nanosized ceramic powders) in the U.S. market is increasing and will jump from $626 million in 1993 to almost $1.1 billion by 2000, according to a study conducted by Business Communications Co. Inc., Norwalk, Connecticut. UFP are being developped for sintering applications as well as for the reinforcement of alloys. As there are many published review papers on ultrafine powders (1-5) and more specifically on thermal plasma UFP generation (6-8), this paper will focus on the SiC ultrafine powder synthesis process, using the inductively coupled plasma.

Ultrafine SiC powders have been prepared in recent years by various investigators and by various methods; e.g. in d.c. and r.f. plasma reactors, using SiC resistance element furnaces or by microwave, laser and CVD techniques. A range of starting materials can be and have been employed in these processes, including solids (Si, SiO$_2$), liquids (CH$_3$SiCl$_3$) and gases (SiH$_4$); methane being the principal carburizing agent used. The variety of combinations of these various SiC formation precursors that have been employed in the different synthesis techniques illustrates the various attempts made to improve some of the following process factors: SiC production rate, degree of conversion, powder quality (i.e. uniform nanoparticle size distribution) and sinterability. In the evolution of processes development leading to ultrafine powder synthesis, a need has always existed to increase the residence time for reactants in the plasma reactor, eg. by such techniques as the Liquid Injection Plasma Synthesis (LIPS) (9) in the case of the d.c. plasma or to obtain the benefit from the natural characteristics of the induction plasma (10). Induction plasma has therefore gained wide acceptance for the synthesis of SiC by process researchers all around the world. Its unique features (no contamination by electrodes, central axis reactants injection, long residence time in the plasma zone, no limitations in the plasma gas chemistry) are all very beneficial to those particular processes that involve the use of low cost, solid precursors. The most widely adopted and typical application for SiC ultrafine powders is the preparation of sintered thermomechanical parts, thus the incorporation of sintering aids such as Boron have been found to be necessary. The technique of induction plasma synthesis for Boron doped SiC has been developped and adapted for the introduction of the required Boron as BCl$_3$ during the SiC vapour phase synthesis. The qualities of powders produced by this process route will be discussed later as a function of the sintering results for various r.f. plasma operating conditions. Silicon Carbide is a widely used material for wear and corrosion resistance, in chemicals pumping and heat exchangers [Sheshadri (11)] as well as potential applications in diesel engines. Apart from producing sintered parts, applications for SiC ultrafine powders are to be found in nanoreinforcement, through the introduction of a second phase of SiC into a matrix material. Mitsubishi Mining and Cement Co., Ltd., Japan have developed a MgO/SiC composite. Potential benefits from the use of SiC nanoparticles could lie in the superplasticity forming process, already developed for zirconia by Lockheed Missiles & Space Co. Depending on the actual ultrafine powder fabrication technique used, any contamination of UFP could be adverse for the eventual sintered products.

The different routes to produce UFP were reviewed by Andrievski (2). He distinguishes physical methods that include gas-condensation in inert or reactive gas and high energy destruction by milling, from chemical UFP preparation by synthesis and thermal decomposition. Physical methods of UFP preparation have been extensively reviewed by Andrievski (2), Gleiter (12). More attention will be given here to the plasma routes. Vissokov et al. (3) published a review of the different plasmachemical technologies for UFP, which does not include SiC. One can however notice that the 5 stages identified by the author for the production of UFP using plasma technology are applicable to SiC: 1. Introduction and mixing of the reactants, 2. Heating/melting and vaporization of the solid phase, 3. Chemical reactions in the gas phase, 4. Quenching which fixes the composition of the desired product, .5. Filtering of UFP by cyclones, mechanical or electro-filters.

INDUCTION PLASMA UFP SIC SYNTHESIS

Gaseous reactants

Due to its very high temperature and high energy density, as well as operating in various atmospheres, plasma techniques are widely recognized as among the most advanced technologies for SiC ultrafine powder production. Synthesis of SiC powders from the $SiH_4 + CH_4$ system is thermodynamically favorable. The practical reaction temperature may be as low as 1200 - 1400°C [Kato et al.(13)]. Vogt et al. (14) prepared ultrafine SiC powder as a ß-SiC pure phase in a thermal argon r.f. plasma, using silane and methane as starting materials. The synthesized particles diameter ranged from 10 to 60 nm, with a specific surface area of 60 to 130 m^2/g but due to extensive agglomeration, the apparent particle size was greater than 0.1 μm. Axial injection of the reactants gave a limited degree of particle size control in the SiC synthesis. By increasing the depth of reactants penetration into the tail flame, the surface area of the powder was increased, reflecting a reduction in the mean particle size. Variations in plate power, reactant feed rates, and the quench gas properties could also affect the powder surface area and mean particle size. Kijima et al. (15) used a 15 kW induction plasma to synthetize ß-SiC UFP with an estimated 6 nm particle diameter. Suzuki et al. (16) prepared $SiC-Si_3N_4$ composite fine powders from chlorosilanes by r.f. thermal plasma. Fig. 1 shows the r.f. plasma torch used. The $SiC-Si_3N_4$ composite fine powders were prepared by injecting chlorosilanes ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2), C_2H_4 and NH_3 to the tail flame of r.f. plasma. Generally, the powders obtained were composed of Si, SiC, Si_3N_4, C and amorphous particles.
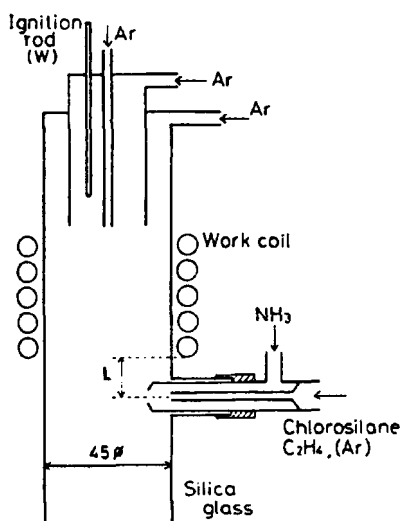

Fig.1 r.f. plasma torch for $SiC-Si_3N_4$
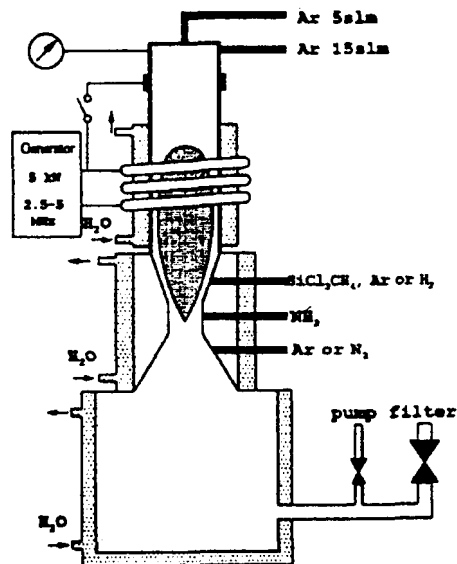composite UFP [Suzuki et al. (16)]

Fig.2 Reactor design for Si_3N_4-SiC
composite UFP [Mach et al. (17)]

The surface area of the powder was from 46 to 100 m^2/g and the particle size was from 20 to 200 nm. SiO_2 was detectable in the powder by XPS. It was found that after heat treatment at 1773 K for 1 h in Ar, the amorphous phase disappeared and the remaining crystalline phases in the powder were SiC and Si_3N_4. The by-product, NH_4Cl, of this process was removed by heating in flowing Ar at 623 K for 1 h. Mach et al. (17) synthesized Si_3N_4-SiC composite powders with an Ar RF induction plasma from $SiCl_4$ and $SiCl_3CH_4$ respectively and NH_3. The reactor design is shown in Fig. 2. The overall particule size distribution is in the range 5-80 nm. Praegraphitic structures decrease with the increase of ammonia flow and or quenching rate. With excess of ammonia, only amorphous powders are produced. Inukai (18) introduced methyl-trichlorosilane diluted with Argon in a 4kW induction plasma. The 20-50 nm diameter

ß SiC powders are associated with traces of α–SiC as well as with free silicon and were collected on the reactor wall. Mitsui and Kato (19) prepared beta silicon carbide powder from the $SiCl_4-CH_4-H_2$ system

using RF-plasma. They studied the effect of reaction conditions on the chemical composition and particle size of the powders. Under the condition of [SiCl$_4$] = 0.1 vol% and [CH$_4$]= 0.13 vol%, the C/Si ratio of the powders increased sharply with decreasing [H$_2$]. The C/Si ratio increased moderately with increase of CH$_4$, and thus the C/Si ratio could be easily controlled by the flow rate of CH$_4$. The crystallite size of the SiC powders had a tendency to increase with increasing reaction temperature. This may be due to a decrease in the supersaturation ratio at higher temperatures.

Induction plasma technology evolution
As extensive use of r.f. plasma has developed in the production of ultrafine powders of various materials, much effort has been also made to improve the r.f. plasma system itself. Hollabaugh et al. (20) developed a high-temperature plasma tube that overcomes the meltdown problem of the water and gas-cooled quartz plasma tubes most commonly used. The r.f. plasma system consists of the plasma tube and its associated power generator, a reaction and cooling off chamber, a powder collection system, and a gas-flow control and vacuum system, as shown in Fig. 3. The key feature of this system is the placement of several heavy-walled, water-cooled copper fingers inside a quartz mantle to shield the mantle from the intense radiation of the plasma. These copper fingers not only keep the quartz mantle cool but also transmit, through the induced voltage and current, energy from the primary r.f. coil to the plasma. Ultrafine silicon carbide powder was made by radial injection of silane, methane, and hydrogen into the tail flame of the plasma. The composition of the silicon carbide powder could be varied over a wide range from excess silicon to excess carbon. This was accomplished by adjustments in the feed gas composition and/or the r.f. power. Particle size of the powder, as determined by TEM and BET surface area measurements, was 10 to 20 nm, with a specific area of 100 m^2/g and some chainlike agglomerates were observed. Kameyama et al. (21) also prepared ß-SiC using a dual r.f. plasma torch system. This new radio-frequency (r.f.) thermal plasma system overcomes both the low power efficiency and the unstable induction plasma commonly used. The injection of methane and SiH$_4$ was stoichiometric. High purity SiC was produced The reaction mechanisms as explained by Kameyama are: Si + SiC$_2$ -->2SiC in the periphery and Si+C-->SiC in the central high temperature zones.
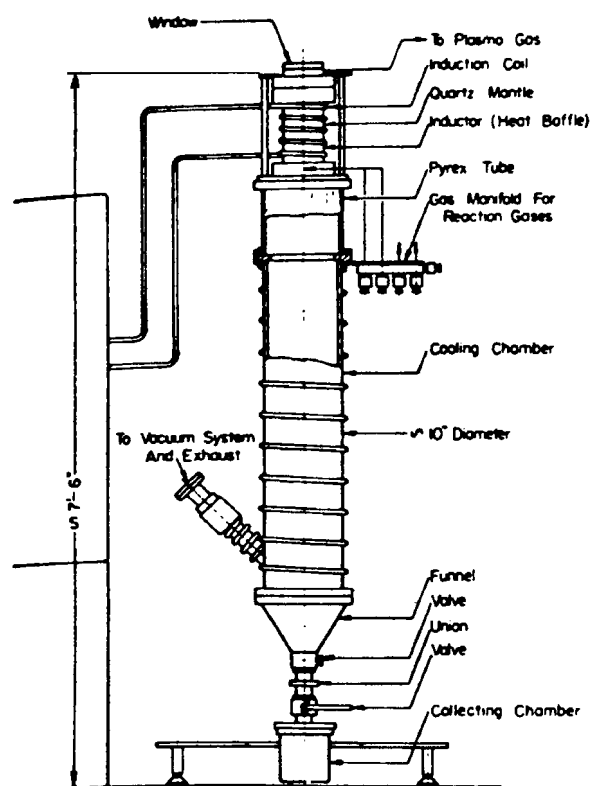

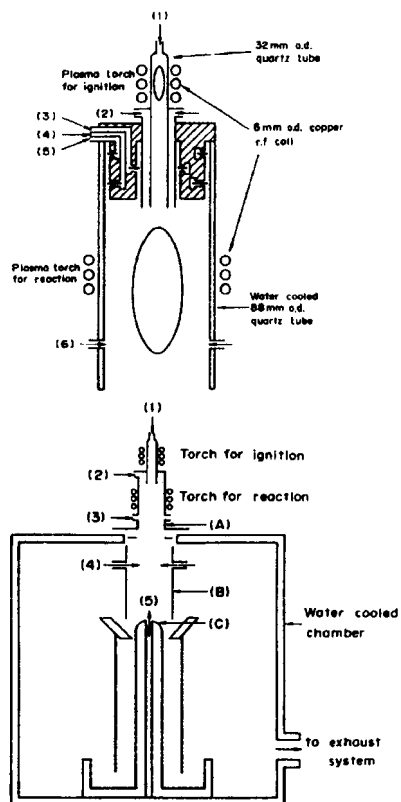Fig.3 Induction plasma UFP reactor
[Hollabaugh et al. (20)]

Fig.4 Dual r.f. torch system
[Kameyama et al.(21)]

The key features of this system are the application of all solid state type r.f. power supply units and the superposition of a small ignitor (0,7kW) r.f. - plasma onto the main r.f. - plasma. High power efficiency (over 75%) was obtained with the all solid state type r.f. power supply units of 30 kW at 3 MHz. Mixed reactant gases of CH$_4$ and SiH$_4$ are introduced into the upper part of the main plasma flame from port [2] with the argon carrier gas, as shown in Fig. 4. Powders formed were deposited on the following three

places: the wall of the plasma torch [A], a collector quartz tube [B] and a copper cylinder [C] cooled with water. Quenching gases following reaction are also able to be fed in from ports [3], [4] and [5]. Small amounts of amorphous powders were deposited on the inner wall of the main plasma torch, i.e. at the place shown in Fig. 4 [A]. In the product amorphous phases, SiC, SiH, CH and SiCH3 species were detected by IR spectroscopy. On the other hand, powders collected at [B], and [C] in Fig. 4 were fully crystalline.

Yoshida et al. (22) developed the "hybrid" plasma concept which is characterized by the superposition of a radio-frequency plasma and a d.c. arc jet and applied it to synthesize SiC ultrafine powders. Lee et al. (23) synthesized ultrafine Si_3N_4 and Si_3N_4 + SiC mixed powders through the thermal plasma, chemical vapor deposition (CVD) using a hybrid plasma, as shown in Fig. 5. The reactant, $SiCl_4$, was injected into the arc jet and completely decomposed in the hybrid plasma, the second reactant, CH_4 and /or NH_3, being injected into the tail flame through multistage ring slits. For the preparation of Si_3N_4 + SiC mixed powders, the N/C composition ratio and particle size could be controlled not only by regulating the flow rates of the NH_3 and CH_4 reactant gases and the quenching gas, but also by adjusting the reaction volume. The results of this study provide sufficient evidence to suggest that multistage injection is very effective for regulating the condensation process of fine particles in a plasma tail flame.
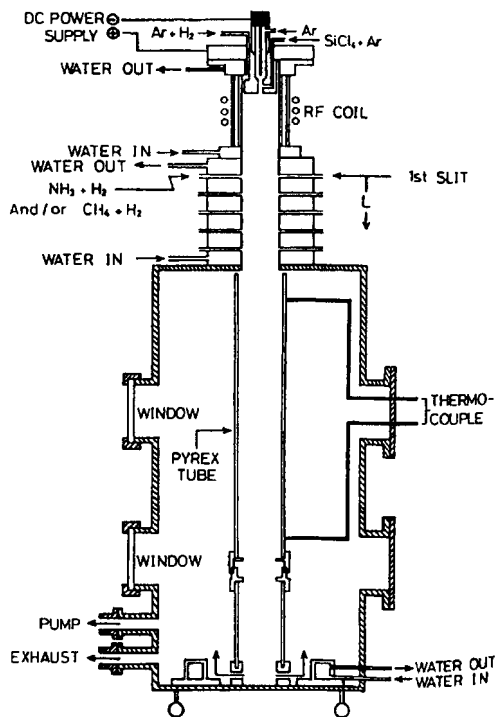

Fig.5 Hybrid plasma system [Lee et al. (23)] plasma

Fig.6 Schematic of the triple convergent d.c. [Kondo and Saiki (33)]

Solid SiC precursors

The use of solid starting materials for SiC powder preparation by plasma includes: CH_4 and SiO_2 in an r.f. induction-produced plasma [British Titan Products Co.(24)], SiO_2 and carbon in a consumable electrode [Kuhn, (25)], Metallic Si and CH_4 in a transferred arc plasma [Ando et al., (26)]. Kong et al. (27, 28) described the production of silicon carbide in an argon plasma jet reactor (confined jet) operated at power levels of 22 kW. Either SiO_2 powder (44 μm in size) or laboratory produced SiO was used as the starting material, with methane serving both as the carrier gas and as the reductant. Some other plasma systems have also been used with solid precursors of SiO_2 or Si: Inoue et al. (29); Nariki et al. (30); Tanaka et al. (31).

Synthesis of UF SiC has been performed by Stachowicz et al. (32) with "rice hulls" used as the raw material. Rice hulls contain finely distributed silica and active carbon which acts as a C source for SiC formation. Unreacted silica and excess of carbon was found to be present in the ß-SiC powder. The various reactions which occur at high temperature between SiO_2 and C are also discussed in this paper. 10 to 20 nm UFP were produced with a 20 kW r.f.reactor. Powder post treatment consisted of carbon removal by oxidation in air followed by silica removal by HF leaching.

In recent years, a number of studies have been performed to synthesize boron-doped SiC ultrafine powders under plasma conditions. Improvements of the SiC UFP synthesis process should lead to lower sintering temperatures, higher densities with smaller and more uniformly distributed grains, as well as few if any uniformly distributed micropores. Kondo and Saiki (33) developed a two-step process for
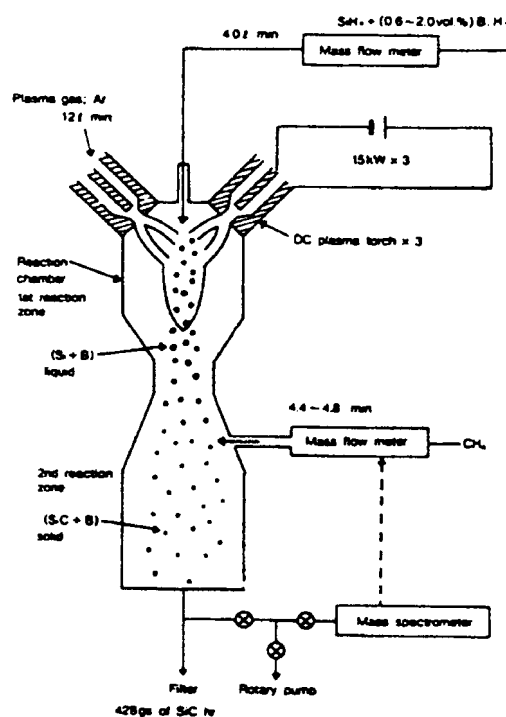
synthesizing boron-doped SiC powders using the arc plasma method. In this process, the reaction chamber was divided into two reaction zones, in which the reaction conditions were independent of each other. Powders were synthesized in two steps: 1) nucleation and growth of the boron containing spherical molten silicon particles, and 2) carbonization of the molten silicon particles. Premixed gases of SiH_4 + (0.6 - 2.0 vol.% B_2H_6) were supplied and injected into the conjunction of three d.c. plasma jets in the first reaction zone. Even though, this method does not involve induction plasma technology, the method used has some of the characteristics of r.f. plasma as seen from Fig. 6. It was proposed that the following phenomena take place in the reaction zone: the supplied gases enter the combined plasma jets to be thermally decomposed to vapors of silicon and boron, and spherical, molten silicon particles, containing uniformly distributed boron, nucleate and grow as the vapors of silicon and boron condense in the cooling plasma gases. Boron-doped SiC powders, with a size range of 0.3 to 0.5 μm, were synthesized from the molten silicon particles by injecting CH_4 gas into the second reaction zone. The powders were collected in a bag filter behind the chamber. One of the reasons for dividing the synthesis process into two steps was proposed as follows: the injection of CH_4 gas together with SiH_4 + B_2H_6 gases into the first reaction zone generates mixtures of SiC, carbon and silicon particles. The amount of the SiC particles, however, was less than 90% of the product mixtures and the particle sizes were much finer. Another factor for consideration was that nucleation of silicon and boron might take place separately; particles of SiC and B_4C, for example, might subsequently develop separately, as a result. In such a case, the SiC powder with boron uniformly distributed in each particle would not be obtained. From this viewpoint, the objective guiding the preparation of inflight doped powders is the production of high purity, spherical or equiaxial powders, with uniform dispersions of additives in the SiC UFP and a narrow size distribution. Carbone and Rossing (34) and Baumgartner and Rossing (35) reported on the synthesis and pressureless sintering of B-doped SiC powders from the $SiCl_4$ + CH_4 + BCl_3 and the $SiCl_4$ + $H_xC_yCl_z$ + BCl_3 reaction systems, respectively, using d.c. plasma.

HEAT AND MASS TRANSFER

Plasma transport properties, as well as the momentum and heat transfer phenomena in plasma reactors, have been widely reported in the literature. However mass transfer has received little attention since the pionnering work of Dundas (36) and Barnes and Nikdel (37). Mixing studies are very important to obtain basic understanding of the species distribution and concentration in the plasma gases and recently, Rahmane et al. (38) and Soucy et al. (39, 40) have conducted several mixing studies on the induction plasma synthesis process by the injection of a tracer gas. The results have show that mass transfer is essentially achieved by molecular diffusion in the highest temperature regions whereas at lower temperatures, turbulence takes over and the mixing of the gases becomes very rapid. Cold gas injection has also been studied with radial as well as axial injection geometry as a function of the gas velocity and injector design.

INDUCTIVELY COUPLED PLASMA SIC UFP SYNTHESIS AT THE CRTP

Historical review
Laflamme (41) has considered various SiC reaction precursors (SiO_2, $SiCl_4$, Si) but his experimental work used elemental Si because a prior thermodynamic equilibrium and kinetic study showed that the silicon carburization is favored at temperatures higher than the melting point of Si Fig. 7, while the kinetic study, as presented in Fig. 8, shows that in less than 1 msec. at temperatures over 2400K, the carburization of the Si vapor is already complete. In order to increase the silicon vaporization rate, the reactor design evolved from a simple Si powder injection in the DC plasma to a rotating cylindrical reactor, with a liquid Si film trapped by centrifuged force and evaporated by the central plasma jet.
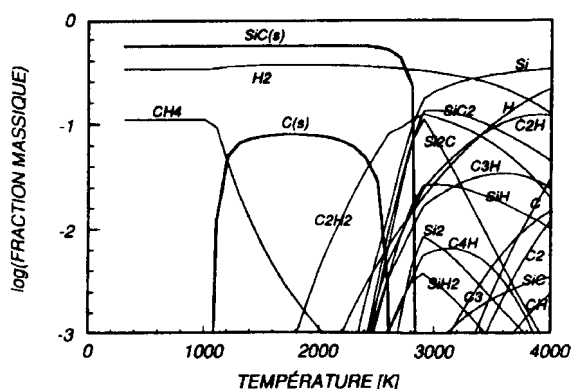

Fig. 7 Thermodynamic equilibrium of Si-C-H at 101.3kPa CH_4/Si=1.5; H_2/Si=10 ( )
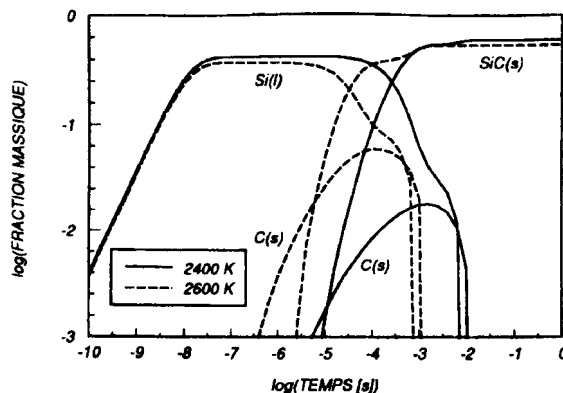
Fig. 8 Mass fraction as a function of time for CH_4/Si=1 id. Fig 7 after Laflamme(41)

Guo (42) followed Laflamme's work with a dry powder collection method and a modified Laflamme rotating reactor. The UFP collected on the metallic filter had a particle size range from 16 to 30 nm with corresponding specific area of 60 to 120 m^2/g from a 35 kW DC plasma. However, severe limitations of the vaporization rate to as little as from 1 to 3 g Si/min were encountered because of the formation of a dense Si vapor layer around the molten pool, limiting further heat transfer to the pool. Furthermore, the reproducibility and the control of the process was poor (free Si and free C accumulated in the SiC powder). The use of induction plasma technology with injected Si was then subsequently considered.

Induction plasma synthesis of SiC research progress
The simultaneous axial injection of Si and CH_4, together with the long reactants residence time in the plasma zone and the large plasma volume are all desirable for the evaporation and reaction processes to proceed in the high temperature zone of the overall plasma volume. The experimental setup employed is presented in Fig. 9. Typical powders collected from the filter are shown in Fig. 10. The measured powder size range was from 40 to 80 nm, with purities trending to 98 % SiC. Powders collected from other system parts were found to be mixtures of SiC, spheroidized silicon, unreacted free silicon and free carbon. By appropriate selection of the experimental parameters, a conversion of 91 to 92 % was obtained, using 30 µm mean particle size input Si, at 50 kW plate power.
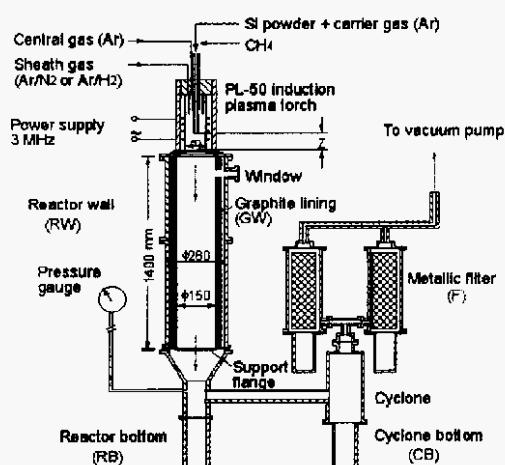

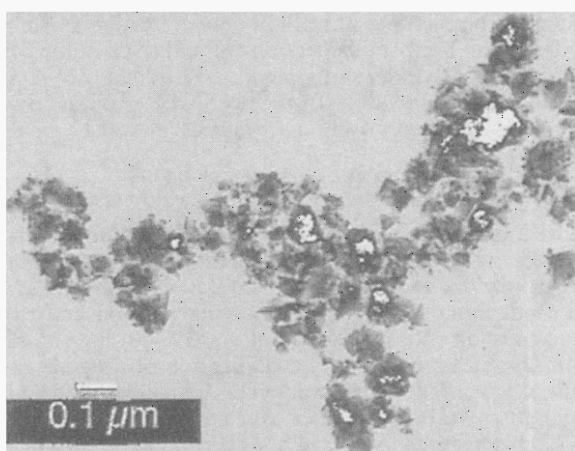Fig. 9 Reactor set-up for induction plasma SiC UFP synthesis after Guo (42)

Fig. 10 SiC UFP collected on the filter [F] Guo (42)

Reaction mechanisms proposed are based on gas phase reactions. Once the powder is injected, the melting of Si begins (Si spheres are present on the reactor wall), but no reaction with the dissociated methane is taking place. The spheres do not show any detectable presence of SiC on their surface. Moreover, preliminary evaporation tests with 60 µm Si particles produced 30 to 40 wt% of evaporation. CH_4 co-injected with the Si does not change this evaporation percentage. With smaller (30µm diameter) Si starting powder, the evaporation percentage increased to 90%. This increase is associated with the absence of SiC on the surface of the Si spheres and proves that the SiC formation is a gas phase process.

A parametric study has also been made by Guo (42) in which he demonstrates that the processing parameters such as the plasma power level, plasma gas composition, reactants injection probe position, feed rates of injected Si and the C/Si molar ratio, significantly affect the conversion and the quality of the SiC powder obtained.

In-flight SiC Boron doped UFP has also been produced by Guo (42) using the same system as described previously and with BCl_3 co-injection. The advantage of Boron in-flight doping has been well demonstrated by Guo, achieving an improvement of the sintering of SiC UFP compacts. However, these powders had sintering volume shrinkage as high as 24%, with a 15% weight loss. The residual Cl content as well as the evaporation of volatile Boron oxide (B_2O_3) are the principal reasons for these volume and mass changes.

                           VAPOR PHASE UFP FORMATION

The different techniques described previously which involve induction plasma UFP SiC synthesis are all gas phase reactions. Thermodynamic and kinetic aspects of the homogeneous nucleation of vapor condensation was extensively discussed by Mc Donald (43, 44). Homogeneous nucleation needs a high degree of supersaturation, with a large number of nuclei required to be created [Abraham (45) and Springer (46)]. Girshick et al. (47) have shown that in the condensation area of the plasma reactor, gas temperature can drop at rates of 10^4 K/s, which makes the homogeneous nucleation the predominant mechanism.

Kato (48) mentionned that the nucleation rate is very sensitive to the supersaturation ratio (SR). When SR increases from 4 to 5, the nucleation rate increases from 10^{-10} to $10^{-0.7}$ with the following equation of formation of UFP $C_{(s)}$ with $A_{(g)}$ and $B_{(g)}$ being the precursors.

$$a\,A_{(g)} + b\,B_{(g)} = c\,C_{(s)} + d\,D_{(g)} \qquad (1)$$
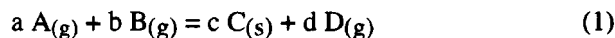
SR can be derived in terms of the thermodynamic quantities:

$$SR = [P_A^a P_B^b / P_D^d]_{react} / [P_A^a P_B^b / P_D^d]_{equil} \qquad (2)$$

$$SR = K\,(P_A^a P_B^b / P_D^d)_{react} \qquad (3) \qquad \text{Kato (48)}$$

where K is the equilibrium constant for reaction (1). K is related to the homogeneous gas reaction UFP production. Kato (48) mentionned that a large K should be related to high reaction rates. Plasma technology is very well adapted to provide the high temperature necessary to increase the reaction rate. Numerical analyses of the nucleation and growth of UFP have been proposed by Girshick et al. (49, 50), Proulx et al. (51), Bilodeau et al. (52), all found good agreement between their computed and experimental data.

CONCLUSION

The UFP production of SiC by the induction plasma technique has been reviewed with the emphasis on the various precursors used, and the different technological choices. As the formation of UFP in the plasma involves complex mechanisms, there is a need for an interdisciplinary approach, with researchers working in diagnostics and modelling, as well as materials specialists for the powder quality evaluation. From the economics point of view, when production of high purity, high specific area SiC powder is desired, metallic Si, with a particle size smaller than 30 μm, is an attractive precursor, using methane as the carburizing agent, coinjected with the powder Si in an induction plasma. As the modelling of the thermodynamic and kinetic phenomena involved in the induction plasma reactor is progressed and it can satisfactorily describe some experimental data, the design of plasma reactors will benefit greatly from this knowledge, and in consequence, the operational scale-up of some of the reactors described in this text for industrial production can be achieved!

ACKNOWLEDGEMENT

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