

R.F.-plasma system for the production of ultrafine, ultrapure silicon carbide powder

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A new high-temperature plasma tube has been developed that overcomes the meltdown problem of the conventional water- and gas-cooled quartz plasma tubes commonly used. 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. The copper fingers act as transformers to couple the plasma to the field of the coil. This new system has been used to produce ultrafine, ultrapure silicon carbide powder.

1. Introduction

Radiofrequency (r.f.) plasmas at atmospheric pressure have been used more extensively in recent years for producing ultrafine powders of various materials. In 1969, Audsley and Bayliss [1] studied the oxidation of silicon tetrachloride in an argon/oxygen plasma and, a year later, Dundas and Thorpe [2] described the production of titanium dioxide by oxidation of the chloride again in an r.f. plasma. Synthesis of several refractory materials in r.f. plasmas was reviewed by Hamblyn and Reuben [3]. More recently, Yoshida *et al.* [4] have made ultrafine titanium nitride in an r.f. plasma and Stroke [5, 6] has described a process for producing silicon carbide powder. Hagawa *et al.* [7] have made ultrafine magnesium oxide by spraying an aqueous solution into a plasma.

Even though the r.f. plasma provides a very clean system and produces very pure powders, it has proven difficult to operate. The prevalent design includes a water- and gas-cooled quartz containment vessel surrounding the plasma and quite often a nonsymmetric condition develops resulting in meltdown of the quartz vessel.

A recent development at the Los Alamos National Laboratory has solved this problem with r.f. plasma equipment and opened the way for further advances in their use. This new system is presently being used to produce ultrafine, ultrapure silicon carbide powder.

2. R.F. plasma system

The r.f. plasma system developed at Los Alamos consists of the plasma tube and its associated power generator, a reaction and cool-down chamber, a powder collection system, and a gas-flow control and vacuum system as shown in Fig. 1.

The key to successful operation of the system is the plasma tube which is a new design using the concept of a transformer. Several heavy-walled, water-cooled copper fingers are placed inside the quartz mantle to shield it from the intense radiation of the plasma. These fingers not only keep the quartz mantle cool but also transmit, through induced voltage and current, energy from the primary r.f. coil to the plasma.

A more detailed view of these fingers is shown in Fig. 2. The chevron cross-section and interlocking of the fingers prevents direct radiation from the plasma to the quartz wall, thereby keeping the quartz mantle cool. Also, the absence of ionizing radiation around the r.f. coil suppresses the troublesome arcing that sometimes occurs between turns and between the coil and the quartz.

In this system, the plasma is fired by evacuating the chamber to a pressure below 0.1 torr, adjusting the plate voltage of the 450 kHz r.f. generator to 6.0 kV, and finally introducing a small amount of argon into the plasma tube. Once lit, the

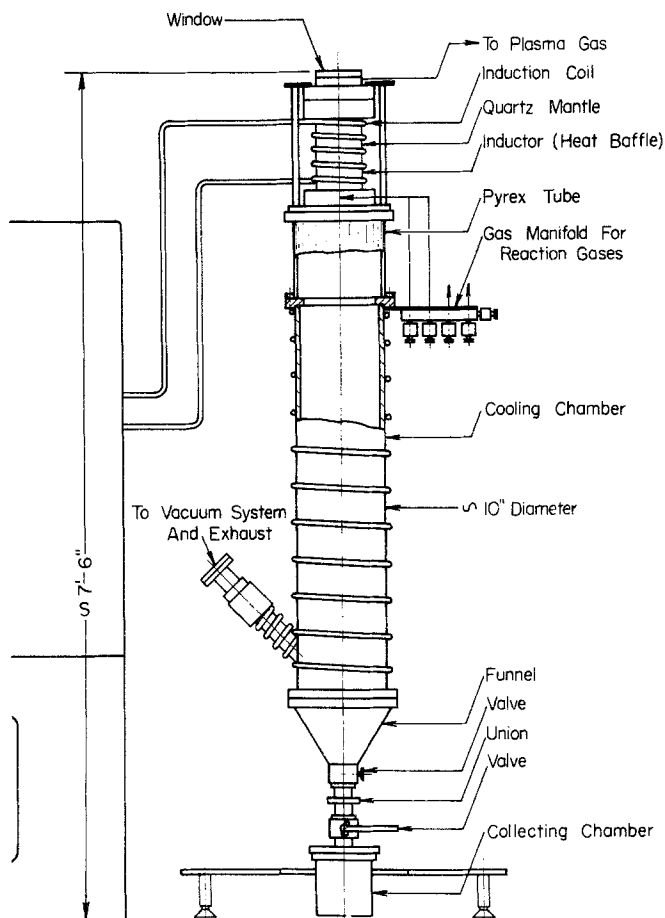


Figure 1 R.F. plasma system for production of silicon carbide powder.

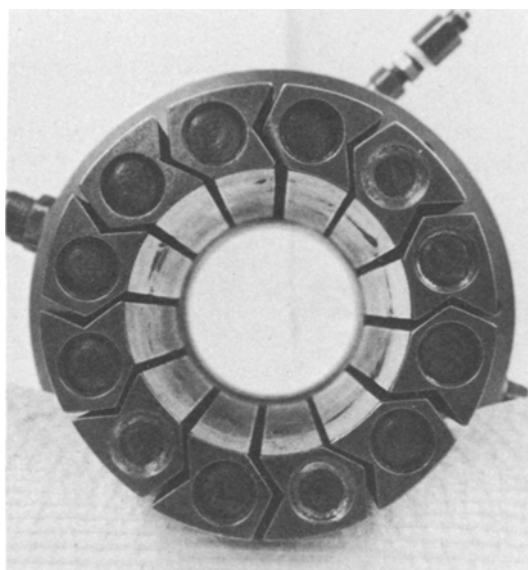


Figure 2 End view of plasma tube fingers.

vacuum valve is closed and the pressure increased to ambient. A minimum argon flow of about 15 SLPM through the plasma provides a tail flame at the bottom end of the plasma tube to heat the reactant gases and to stabilize the plasma.

The 250 mm diameter reaction tube chamber sits immediately below the plasma tube. In the upper section, the reactant gases (silane, methane, and hydrogen) are injected into the plasma tail flame through four injection ports arranged orthogonally around the lower end of the plasma tube. Here the gases are heated to a high temperature and upon subsequent rapid cooling, become supersaturated and precipitate silicon carbide. Because of the very rapid cooling and high supersaturation, the number density of nuclei is large and particle growth is limited. These conditions produce ultra-fine powder (approximately 10 nm size particles). A borosilicate glass bell jar surrounds this section to permit viewing of the plasma flame. During

powder production, however, the inside wall of the glass becomes coated with a powder deposit during the first 3 to 5 min so that continued viewing is not possible.

Below the reaction chamber is a water-cooled, cool-down chamber of the same diameter as the reaction chamber. Here the gas/powder mixture is cooled to ambient temperatures. A considerable amount (about 45%) of the powder collects on the walls of this chamber and cannot be utilized because of subsequent oxygen contamination when the system is opened up to cleaning.

A sampling device is connected to the bottom of the cool-down chamber through a 25 mm valve. A powder sample is taken by vacuum transfer. Special precautions are needed to maintain an inert atmosphere because of oxygen contamination upon exposure to air.

Near the bottom of the cool-down chamber, a 50 mm exhaust line carries the gases and entrained powder to the powder collection system. The powder collection system consists of two cyclone separators in series. Although the basic particle size is less than 25 nm, much too small to be separated by a cyclone separator, there is enough agglomeration for efficient separation and collection. Over a 4 to 6 h running time about 45% of the powder collects on the walls of the reaction and cool-down chamber, 45% in the cyclone separator, and the remainder is lost in the exhaust. Production rates of 100 g h^{-1} have been achieved but this was limited by the gas metering system and not the plasma capacity.

3. Results and discussions

3.1. Plasma characteristics

The r.f. plasma tube developed at Los Alamos has been operated at several frequencies from 450 kHz to 3.0 MHz at power levels from 15 to 50 kW. The copper fingers are effective in keeping the mantle cool and transmitting power from the coil to the plasma. The plasma ball itself is typical of those found in a quartz system. If viewed from the top of the plasma tube, the plasma ball has a small dark spot about 10 mm in diameter at the centre, presumably due to poor coupling along the central axis. This central cool area is surrounded by a doughnut of hot plasma, which extends radially to within 10 to 15 mm of the fingers. The area immediately adjacent to the fingers is cool.

The reason for this cool annulus between the plasma and the copper fingers is not known but

we believe that the heat loss to the fingers might be enough to keep the gas temperature below its ionization point such that the gas in the annulus would not couple to the r.f. field and, consequently, no power would be generated here. Because of the heat loss, the minimum power required to sustain the plasma is about 13 kW at ambient pressure (590 mm Hg in Los Alamos) with pure argon. At lower power levels the plasma tends to shrink and go out.

At a fixed argon flow through the plasma, the length of the tail flame can be increased by increasing the power up to a certain point. Beyond this point, the plasma again begins to shrink due to magnetic pinch and be extinguished as the power is increased further. But even at these high power levels, greater than 30 kW, the plasma can be expanded by increasing the gas flow. Thus by adjusting both gas flow and power, power levels up to 50 kW have been achieved.

3.2. Silicon carbide powder synthesis

Ultrafine/ultrapure silicon carbide powder was made by radial injection of silane, methane, and hydrogen into the tail flame of the plasma. We have done preliminary studies of the effects of gas composition and r.f. power on the chemical composition of the powder and have evaluated the particle size and crystal structure of the powder.

The composition of the silicon carbide powder can be varied over a wide range from excess silicon to excess carbon. This is accomplished by adjustments in the feed gas composition and/or r.f. power. Table I lists the power and gas flows for several different conditions. The plasma argon is used to sustain the plasma and to provide the tail flame. The process argon is used as a diluent for the process gas which is injected into the plasma tail flame. In the first three runs at power levels between 15 and 19 kW, the only change made was in the silane flow rate. Chemical analyses of Runs 1 and 2 were not made but the colour comparison of Runs 1, 2, and 3 clearly showed the differences. Run 1 was a dark tan colour, Run 2 black, and Run 3 dark grey. In addition, visual examination of Run 1 at 50 \times showed some spherical particles that were not present in the other two runs; also, X-ray diffraction of powder from Run 1 gave patterns for silicon as well as beta-silicon carbide. We believe these spheres to be silicon. The excess carbon in Run 2 did not

TABLE I Process variables and powder composition

Run number	Power (kW)	Plasma argon	Process gas flow (SLPM)				Powder composition
			Process argon	Hydrogen	Methane	Silane	C/Si ratio
1	15	22	4.5	5.3	1.0	0.65	Excess Si
2	15	22	4.5	5.3	1.0	0.21	Excess C
3	19	22	4.5	5.3	1.0	0.41	1.1
4	18	34	4.5	5.3	2.3	0.65	1.0
5	33	34	4.5	5.3	1.0	0.41	1.9

produce an X-ray pattern and is presumably amorphous carbon. All three runs contained beta-silicon carbide as the major constituent. The chemical analysis of Run 3 showed that the carbon-to-silicon ratio was 1.1 or very nearly stoichiometric.

In Run 4, the plasma argon was increased simultaneously to an increase in both methane and silane. This change produced a carbon-to-silicon ratio of 1.0 at the same power level as the first three runs.

In Run 5, the power level and plasma argon flow were increased, but the other gas flows were the same as Run 3. Here the carbon-to-silicon ratio in the powder increased to 1.9, almost doubling that of Run 3. While these data are certainly not conclusive, they suggest that higher power levels increase the carbon activity in the gas providing more carbon for incorporation into the powder.

Hydrogen in the feed gas lowers the temperature

of the tail flame considerably. This is illustrated by the observation that with only plasma and process argon flowing, a visible tail flame extends approximately 100 mm into the reaction chamber. The introduction of only half of the hydrogen used in these experiments will quench the visible part of the tail flame, a clear indication of a large drop in temperature. It is not surprising then that a change in power will have a major effect on the reactions in the tail flame because of temperature changes.

Particle size of the powder was determined by transmission electron microscopy. Fig. 3 is a photomicrograph of some of those particles showing a particle size of 10 to 20 nm. The chain-like agglomeration is characteristic of particles in this size range, although the manner in which the individual particles are bonded together is not get know. These sizes are consistent with a BET surface area measurement of $101 \text{ m}^2 \text{ g}^{-1}$ (equivalent to a particle diameter of 18.5 nm).

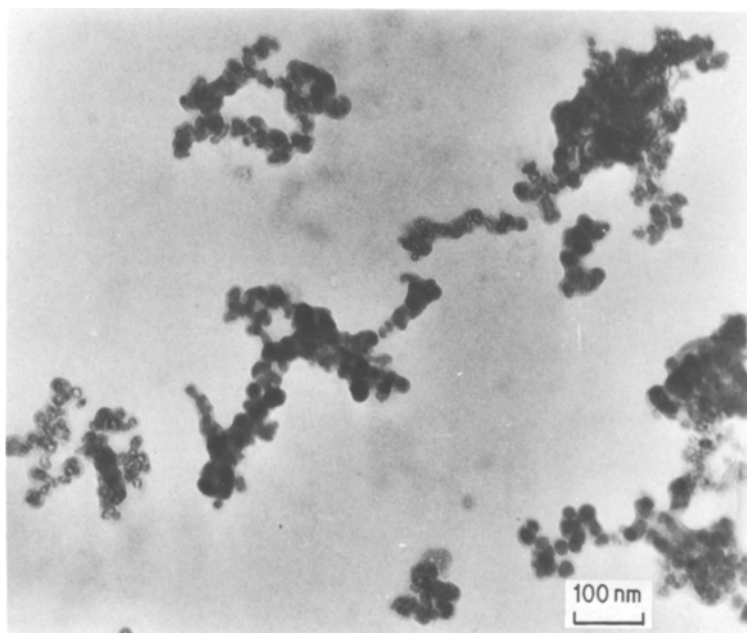


Figure 3 Transmission electron micrograph of silicon carbide powder.

X-ray diffraction results indicate a domain size of 7.5 nm and a crystal structure of beta-silicon carbide. Since the structure is the beta-phase, this in itself suggests a fairly low temperature of 2600 K or less.

It is interesting that although the basic particle size is much too small for collection in a cyclone separator, a very efficient separation can be done because of the agglomeration that occurs. Almost 90% of the silicon carbide is collected either on the walls of the cool-down chamber (approximately 45%) or in the cyclone separator (approximately 45%). The remaining 10% is lost in the exhaust mostly as smoke. We believe that most of this smoke could be collected on a suitable filter.

One of our objectives in doing this work was to produce ultrapure silicon carbide. Spectrographic analysis of these powders shows that the impurities are well below those of good commercial powders. Table II lists the impurities of powder made at Los Alamos compared to an H. C. Starck Company Grade B-10 silicon carbide powder. With the exception of zinc, all impurities are present at concentrations lower than in the commercial powder. Elements not listed are below detectable limits.

As with most high-surface area and chemically active materials, oxygen contamination is a problem. The oxygen content of these powders as sampled in the process and maintained in an argon atmosphere is less than 0.5 per cent by weight. Various exposures to air can increase that to 3.0 per cent. Consequently, special handling procedures are required to maintain a low oxygen content.

4. Conclusions

An r.f. plasma tube has been designed that is very reliable and overcomes the problems of overheating in the conventional plasma systems. This new plasma system has been used to produce ultrafine, ultrapure silicon carbide powder, and shows substantial promise for similar developments in other ceramic systems.

TABLE II Impurity composition of the powder compared with commercial powder

Element*	CVD powder	Commercial powder†
B	<10 ppm	200 ppm
Al	10	800
Ca	5	50
Ti	<3	50
Cr	<10	20
Fe	<10	300
Cu	20	40
Zn	100	<30
Ag	5	<1
W	<300	1000
O	<1%	Unknown

*Elements not shown are below detectable limits for both powders.

†H. C. Starck Company – Grade B-10.

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