

# The manufacturing of nanoparticles with a plasma process

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## Synopsis

Non-transfer-arc linear plasma systems are highly suited to manufacturing nanoparticles. In this paper, the manufacturing of such particles with specially designed plasma systems is discussed. In general, it entails the volatilization of a metal halide that is injected in the high-temperature region of a plasma flame, where it is reacted with a suitable reagent, for example  $O_2$ , to produce nanooxide powders. Metal powders can also be introduced directly in the plasma. Due to the very short residence time of only milliseconds in the reaction zone, as well as the fact that the reaction takes place in the gas phase, combined with very rapid quenching in the order of  $10\ 000^{\circ}C.s^{-1}$ , nanoparticles are produced. At Necsa the manufacturing of such particles has been demonstrated on various scales. A pilot plant for the production of nano- $Al_2O_3$ , and two pilot plants, one using  $SiCl_4$  and the other one using  $SiF_4$  as feed material, were built to produce fumed, pyrogenic, nano- $SiO_2$ . The alumina plant had a production rate of  $8\text{--}10\ kg.h^{-1}$  and the silica plants had production rates of 2 and  $10\ kg.h^{-1}$  respectively. Perfectly spherical alumina particles with a particle size distribution of between 10 and 200 nm were produced on a continuous system. Particle size analysis for the silica by SEM measurements showed a  $d_{50}$  of 60 nm and a particle size distribution of 30–100 nm. The specific surface area was in the range of  $170\ m^2.g^{-1}$ . Other samples of plasma produced nanoparticles such  $ZnO$  and  $B_4C$  will also be presented.

synthesis.<sup>1</sup> Since the temperatures of thermal plasmas are extremely high ( $>10\ 000^{\circ}C$ ), the chemical reactions and kinetics are much more energetic than those encountered in conventional processes. At these high temperatures, the species are mostly present in the fundamental state or as radicals, which make the plasma process chemically unspecific, thus allowing the synthesis of new compounds from the atomic level.<sup>4</sup> Also, the very rapid quenching rates of the product powder ( $>10\ 000^{\circ}C.s^{-1}$ ) prohibit crystal growth and result in the formation of nanoparticles. The high quenching rate nucleates particles before the vapour impinges on the cooled walls of the plasma reactor. The supersaturation of the vapour species due to the high quenching rate provides the driving force for particle nucleation. Thermal plasma synthesis offers a one-step process for the production of very small and chemically pure particles. Either the discharge or the plasma flame itself can be used for the synthesis of the nanopowders. In thermal plasma synthesis, the reactants can be liquids, solids or gases, or combinations of them, before injection into the plasma. The advantages of plasma processes include:

- High temperatures and therefore fast chemistry and short processing times for gas-phase reactions (in the order of milliseconds)
- Very little contamination, high purity product
- Rapid quenching ( $>10\ 000^{\circ}C.s^{-1}$ )
- Comparatively small reactors and process equipment (saving in capital costs)
- Controlled atmosphere (either oxidizing, reducing or inert)
- Wide choice of reactants (solid, gas and liquid)
- Continuous process possible.

## Introduction

The development and production of high-quality, ultra-fine or nanoparticles for the high technology ceramics industry is becoming one of the most important and urgent aspects of the nanoworld today. In particular, ultra-fine and nanoparticles and their superior properties find applications in high-tech ceramic materials and it is also of interest in nuclear technology for applications in future high-temperature nuclear reactors.<sup>1,2</sup> Thermal, non-transfer-arc linear plasma systems and their unique processing capabilities, offer the opportunity to produce such particles.<sup>3</sup> High-temperature gas-phase chemistry, within the high temperature plasma environment, the supersaturation of vapour species combined with very rapid quenching rates and steep temperature gradients, have become known as

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The combined advantages were used as the foundation for an innovative design and equipment specialization for the synthesis of nanomaterials at Necsa and Thermtron. Typical processes that were investigated are the following:

- The production of nanooxides, e.g. by the reaction between aluminium and oxygen, or zinc and oxygen, to produce the corresponding nanometal oxides
- Metal halide reactions, e.g. production of boron carbide by the reaction between boron trichloride and hydrogen/methane
- The production of nanosilicon-dioxide (fumed or pyrogenic silica in the nanoparticle size range) by the reaction between silicon tetrachloride and oxygen, or silicon tetrafluoride and steam.
- Compound conversion or decomposition.

The purpose of this paper is to describe processes that were developed in South Africa by Necsa and Thermtron to produce nanoparticles on pilot scale and to show that production of nanoparticles is not on the 'nanoscale' any more and has already reached the level of pilot scale. Therefore, for the purpose of this paper, pilot scale is defined as a complete working system with a production rate of at least several  $\text{kg.h}^{-1}$  with the capability of running continuously on semi-production and commercial principles.

### Production of nanomaterials

The following nanomaterials and processes for their manufacturing will be discussed:

#### Nanosilica ( $\text{SiO}_2$ )

Fumed, nanosized silica powders are used for their thickening, viscosity control, suspension, emulsification and reinforcement properties by industries such as plastics, rubbers and adhesives, paints and coatings, printing inks, pharmaceuticals and cosmetics. Fumed silica ( $\text{SiO}_2$ ) can be produced by the reaction of silicon tetrachloride ( $\text{SiCl}_4$ ) vapour with oxygen at about  $1100^\circ\text{C}$  in a specially designed plasma reactor, according to Reaction [1]:



A pilot-plant facility was established at Necsa to produce nano- $\text{SiO}_2$  at a rate of  $2 \text{ kg.h}^{-1}$  from  $\text{SiCl}_4$  vapour and  $\text{O}_2$  in a 15 kW linear plasma burner system. A process flow diagram of the system is schematically presented in Figure 1. Because of  $\text{SiCl}_4$ 's low boiling point ( $57^\circ\text{C}$ ) and relatively high vapour pressure (33 kPa at  $25^\circ\text{C}$ ), it was transferred from a suitable feeding vessel to the plasma reactor by a controlled flow of nitrogen at room temperature. The  $\text{SiCl}_4/\text{N}_2$  gas mixture was introduced to a water-cooled stainless steel plasma reactor, and heated in a nitrogen plasma tail flame to about  $1100^\circ\text{C}$  within milliseconds (Figure 2). The heated gases reacted with  $\text{O}_2$  in an annular mixing chamber. Rapid quenching of the product and gas stream directly below the reaction chamber to  $<250^\circ\text{C}$  was achieved by the introduction of cold nitrogen gas via an adjustable quench probe. Agglomeration of the ultra-fine, nanoparticles, took place in a coiled pipe heat exchanger prior to collection in a cyclone and bag filter. In this system, chlorine formed during the reaction, was scrubbed out in two standard packed-column scrubbers. On industrial and commercial scale, this chlorine gas will be

recovered and recycled in order to address waste minimization, and add favourably to the economics of the process, with the end in mind of a complete closed cycle.

Amorphous, white, fumed, nanosized silica was collected by the cyclone and bag filters. As determined by SEM analysis (Figure 3), it had a particle size of  $d_{50} = 60 \text{ nm}$ , and a particle distribution of 45–80 nm (Figure 4), with a specific surface area of  $170 \text{ m}^2 \cdot \text{g}^{-1}$  (BET). The product had a chemical purity of  $>99.5\%$ . Purity can be greatly enhanced by optimization of reactor and system material of construction, and the purity of feed  $\text{SiCl}_4$ , but for normal applications, a purity of 99.5 % is usually sufficient. In another project at Necsa, optical and epitaxial-grade  $\text{SiCl}_4$  were produced, which could be used as feed material for very high-purity nanosilica, if required. XRD analysis showed that the nanosilica was highly amorphous.

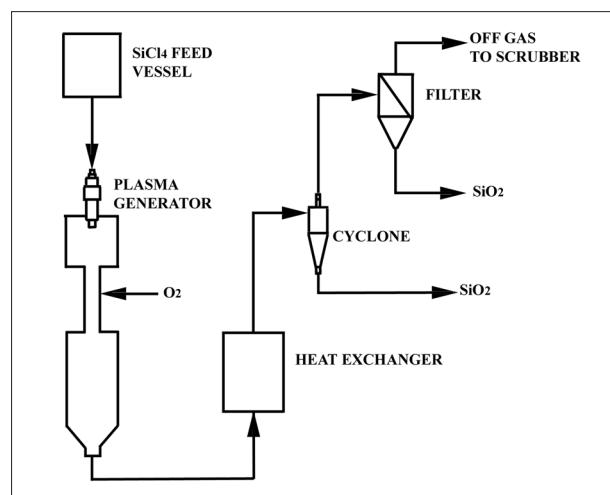


Figure 1—Flow diagram of the nanosilica pilot plant

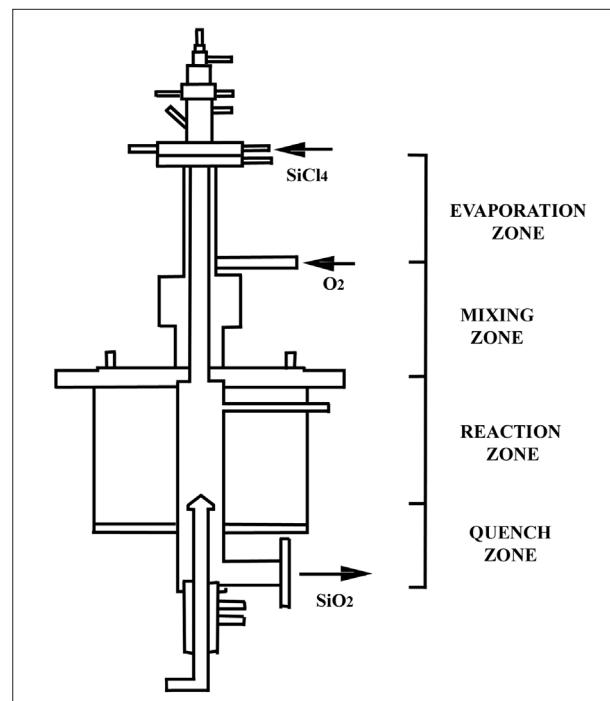


Figure 2—Plasma reactor for synthesis of nanosilica

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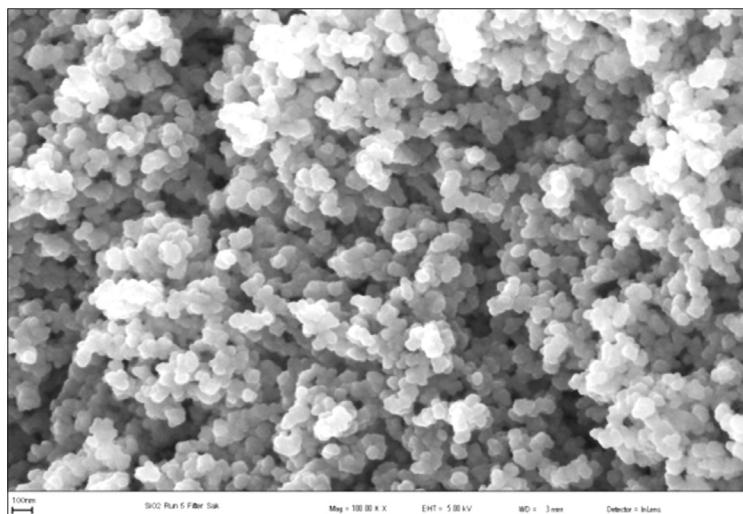


Figure 3—SEM image of nano-  $\text{SiO}_2$  with  $d_{50} = 60$  nm

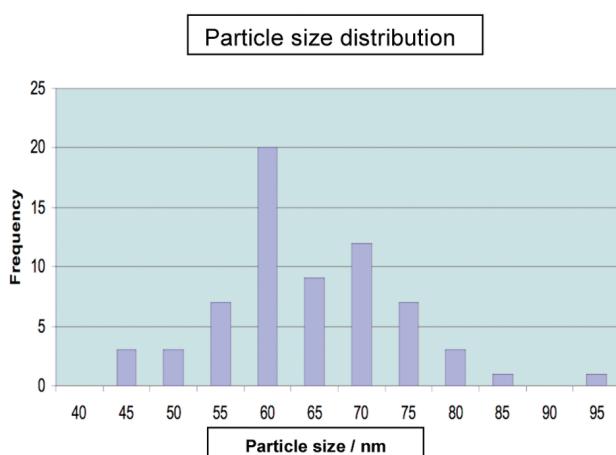
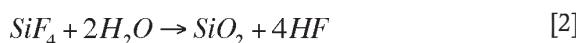


Figure 4—Particle size distribution of nanosilica

In previous work done by Necsa, nanosized fumed silica was also produced by the reaction between silicon tetrafluoride ( $\text{SiF}_4$ ) and an excess of steam in a plasma reactor. Fumed silica was obtained as a secondary product in the recovery of HF from  $\text{SiF}_4$  in the off-gas stream in the plasma dissociation of zircon sands. Pilot-plant experiments were carried out in a 150 kW plasma pilot plant with a nominal capacity of  $12 \text{ kg.h}^{-1}$   $\text{SiF}_4$  feed rate. Fumed, nanosized silica, with a particle size of  $d_{50} = 20$  nm and specific surface area of  $250\text{--}300 \text{ m}^2\text{.g}^{-1}$  (BET) was obtained from the following reaction at  $1200^\circ\text{C}$ :



The challenge posed by this process was to prevent the reverse reaction from taking place between the formed HF and the nanosilica. Thermodynamics dictated that this reverse reaction does not occur at temperatures of  $>600^\circ\text{C}$ . Therefore filtration/separation at these extreme temperatures were necessary and were successfully achieved.

### Nanoalumina ( $\text{Al}_2\text{O}_3$ )

Ultra-fine, nanosized alumina is typically used in catalyst carriers, ceramic membranes, sintering aids, high-temperature lubricants, and particulate-reinforced composites. It can be produced by the reaction between aluminium metal and oxygen at  $1000^\circ\text{C}$ :



Aluminium metal powder ( $75 \mu\text{m}$ ) was introduced to the tail flames of three 30 kW air plasma burners (orientated at  $120^\circ$  to each other) by a piston feeder, where it was evaporated to react with  $\text{O}_2$  downstream of the plasma burner assembly. The product was cooled in a heat exchanger and collected by two high-surface-area membrane bag filters. Pilot-plant experiments of more than 1 hour were conducted on the plant at a production rate of  $8\text{--}10 \text{ kg.h}^{-1}$   $\text{Al}_2\text{O}_3$ . Solid spherical particles of  $10\text{--}200$  nm alumina (Figure 5), predominantly in the delta phase, with a specific surface area (BET), of  $15\text{--}40 \text{ m}^2\text{.g}^{-1}$  were obtained.



Figure 5—TEM image of nanosized alumina (10–200 nm)

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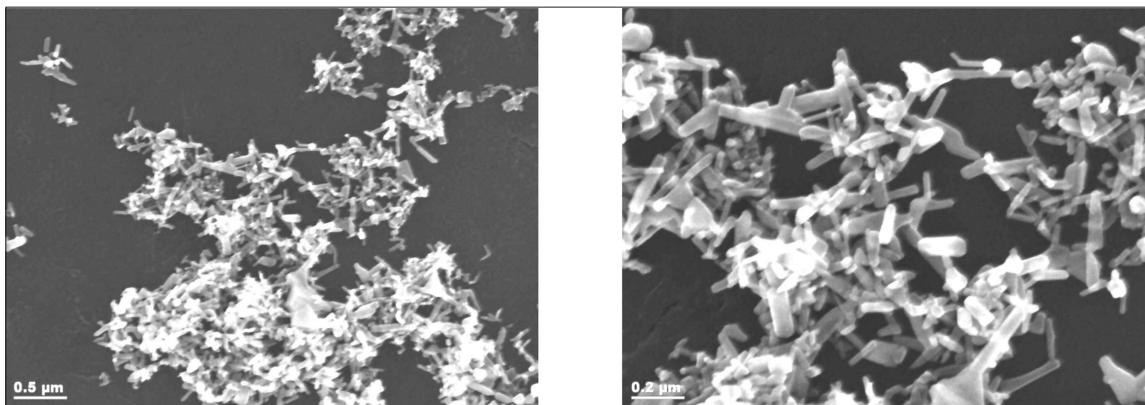


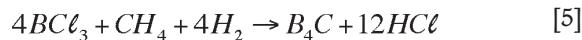
Figure 6—SEM images of nano-ZnO crystals

### Boron carbide ( $B_4C$ )

Because  $B_4C$  has a high neutron absorption cross-section, and is much less expensive than pure boron, it is commonly used as absorbent for neutrons in nuclear applications.<sup>2,3</sup> It is typically produced from  $B_2O_3$  or  $H_3BO_4$  and carbon-containing materials in electric arc plasma furnaces by the following chemical reaction:



Nanosized  $B_4C$  was produced in a 10 kW, 455 kHz radio-frequency induction heater by a lab-scale, batch-mode process whereby a milled mixture of  $B_2O_3$  and graphite was heated in an inert atmosphere. The produced vapours condensed on a cold finger, forming a black precipitate that was characterized as boron carbide with particle size  $d_{50} = 300$  nm. In another attempt to produce nanosized  $B_4C$  for nuclear applications, boron trichloride ( $BCl_3$ ) was evaporated at 60°C and introduced as a vapour at a feed rate of 120  $\ell \cdot h^{-1}$  to a 30 kW plasma reactor, where it reacted with  $CH_4$  and excess  $H_2$  at about 2200°C, according to reaction [5]:



The product mixture was quenched by  $N_2$ , and separated by a cyclone from the off-gas stream. The  $B_4C$  product was analysed by SEM to reveal a particle size of 80–100 nm.

### Nanozinc oxide ( $ZnO$ )

Zinc oxide was one of the first materials to be used in nanotechnology and is greatly utilized in, for example, sunscreens. In addition to crystalline shapes, nanowires and loops may also be fabricated with potential applications in blue lasers, transparent transistors and sensors.  $ZnO$  is also the major hope for the next generation of LED-based solid state lighting. A further area of research is in magnetic semiconductors to serve as the next generation of further miniaturized computer memory.

Nanosized  $ZnO$  was produced in a 30 kW air plasma reactor system at a production rate of 3 to 4  $kg \cdot h^{-1}$ . Zn metal (50  $\mu m$ ) was reacted with oxygen under plasma conditions. After quenching, the product was separated from the gas

stream by a cyclone. SEM analysis revealed needle-like crystals of 200 nm long with a diameter of less than 50 nm (Figure 6).

### Summary

It was proven that powder syntheses of nanoparticles by plasma technology is possible. This was demonstrated on a pilot plant scale at production rates of several  $kg \cdot h^{-1}$ . By utilizing and manipulating the unique properties that plasma technology offers, it was demonstrated that the following nanoparticles can successfully be produced:

- Fumed silica (60 nm), from  $SiCl_4$  at a production rate of 2  $kg \cdot h^{-1}$
- Fumed silica (20 nm), at a production rate of 12  $kg \cdot h^{-1}$  from  $SiF_4$
- Alumina (10–200 nm), at a production rate of 8–10  $kg \cdot h^{-1}$  from the plasma oxidation of aluminium metal
- Boron carbide (80–100 nm) from  $BCl_3$  or  $B_2O_3$
- Zinc oxide (50–200 nm) at a production rate of 3–4  $kg \cdot h^{-1}$  from the plasma oxidation of zinc metal.

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