Nanopowders Synthesis at Industrial-Scale Production Using the Inductively-Coupled Plasma Technology

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ABSTRACT

The increasing demand for nanopowders (particles size <100 nm) having very specific properties calls for the development of new technologies that could bring nanopowders synthesis at the industrial scale. The production of rather large volumes of nanopowders involves processing equipments that can provide a complete control of the synthesis conditions in a continuous producing mode with strong reliability, as well as low processing costs. More importantly, such equipments must be designed to ensure the safe recovery and handling of the ultra-fine constituents. Inductively-coupled plasma (ICP) is one of the most promising approach in the production of a wide range of nanopowders with tailored properties, either at laboratory or industrial scales. The ICP technology developed by Tekna Plasma Systems Inc. will be briefly described, while highlighting specific characteristics that make this technology particularly attractive for the synthesis of various types of nanopowder.

Keywords: Inductively-coupled plasma, nanopowder, production.

1. INTRODUCTION TO ICP TECHNOLOGY

At a sufficient high energy, solids can be melted to liquids and vaporized to form gases, which are ionized to generate a plasma. Plasmas are partially ionized gases containing ions, electrons, atoms and molecules, all in local electrical neutrality. Plasmas can be generated by different means, including inductively coupled plasma (ICP, or induction plasma). ICP are generated through the electromagnetic coupling of the input electrical energy into the discharge medium. More specifically, radio frequency (RF) AC currents in a coil (Figure 1a) generate an oscillating magnetic field that couples to the partially ionized gas flowing through the coil (the discharge cavity), generating thereby a stable discharge [1]. Under typical low power conditions (torch power < 100 kW; oscillator frequency of ~3 MHz), the discharge is found to present a diameter of ~20 – 30 mm (Figure 1b), while for high power industrial installation (torch power > 100 kW; oscillator frequency of 200 – 400 kHz), the discharge volume can reach 50 – 100 mm in diameter by 200 – 600 mm long [2]. These physical parameters represent the basic criterion for the design of Tekna's ICP torches [3].

A selection of ICP torches designed and manufactured by Tekna Plasma Systems Inc. is shown in Figure 1c. The ICP torch consists in a water-cooled ceramic confinement tube surrounded by an induction coil of 3 to 7 turns, which is connected to the RF power supply through the tank circuit. The gas distributor head located on the upstream part of the torch is used for the introduction of different types of gas into the discharge cavity. This specific design allows a particular flow pattern that insures a stable discharge in the center of the coil. A water-cooled stainless steel probe, which is inserted through the torch head, is used to inject the reactants (*i.e.* gaseous species, powders, or liquids) coaxially into the center of the discharge. The temperature at the injection point is typically > 10000 K (see modelling results in Figure 2), even though the plasma is generated at atmospheric pressure or under soft vacuum conditions (*i.e.* down to ~1 psi). The downstream end of the torch is a water-cooled exit nozzle that acts essentially as an interface between the plasma torch and the processing chamber. The shape of the nozzle can be either convergent or divergent, depending on the needs of materials processing.

Because of the unique plasma torch design, the ICP technology arises to be a versatile and reliable processing method that became highly attractive in the synthesis and surface treatments of advanced materials over the last decades. Such growing interest for the ICP technology is mainly due to unique features summarized as follow:

- No electrodes (consumable);
- High purity environment (absence of electrode erosion);
- Axial injection of feedstock in the highest temperature zone of the plasma;
- Rather long residence time within the hot gas stream (up to ~500 ms, depending on the reactor design, in comparison to typically < 1 ms in DC plasma unit);
- Large-volume plasma;
- Discharge in various types of atmospheres, namely inert, reducing, corrosive or oxidizing;
- Rather high throughput.

One of the main advantage of the ICP technology is the processing flexibility regarding the chemistry of the plasma gas. Indeed, the absence of electrodes (as found in conventional DC plasma torches) allows plasma generation not only under inert or reducing environments, but also under oxidizing atmosphere [4]. Depending on the nature of

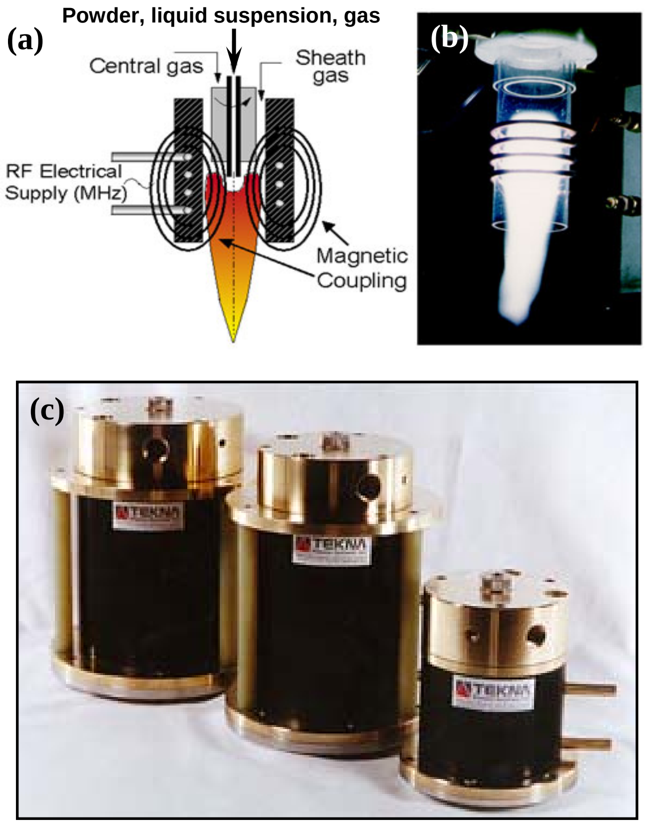

Figure 1: (a) Operation principle of the induction plasma torch. (b) Low power plasma discharge in air. (c) Induction plasma torches manufactured by Tekna Plasma Systems Inc. [3]. From left to right: PL-70, PL-50 and PL-35 (PL-100 not shown). The number refers to the internal diameter (in mm) of the ceramic confinement tube.

the gas mixture injected in the discharge cavity and, more importantly, on the ionization potential of these gases, various torch performances may be obtained. The gas selection is thus found to depend essentially on chemical reactions to be promoted or avoided in the reactor.

2. NANOPOWDERS SYNTHESIS

The versatility of the ICP technology offers the possibility to modify or produce advanced powders at the nanometer scale. Indeed, the powder spheroidization or the nanopowder synthesis can be performed on the same plasma unit, which needs only minor design modifications. Also, the ability of ICP technology allows the processing of a wide variety of advanced materials of specific properties at a relatively high yield and affordable production cost [4]. This convenient technology is well suitable to face the growing interest that arises not only from academic institutions and research centers, but more recently from industries in their search for a reliable and high capacity manufacturing technology. The two fundamental key features that make the ICP technology attractive are the very high temperature processing and the high quench rate. Since the temperature prevailing in the center of the discharge can reach more than 10000 K, reaction rates are much faster than those found in conventional methods. The local temperature remains fairly high over rather long axial distance, corresponding thereby to residence times sufficiently long to enable the evaporation of most materials. As an illustration, modeling works (for instance, see Figure 2) suggest that the on-axis temperature in PL-50 and PL-70 torches rises above 2000 K for typically 500 ms, and is found to exceed 4000 K over the first ~50 ms. On the other hand, the high quench rate at the exit of the reactor, which is typically ~10^5 K/s, prevents products dissociation

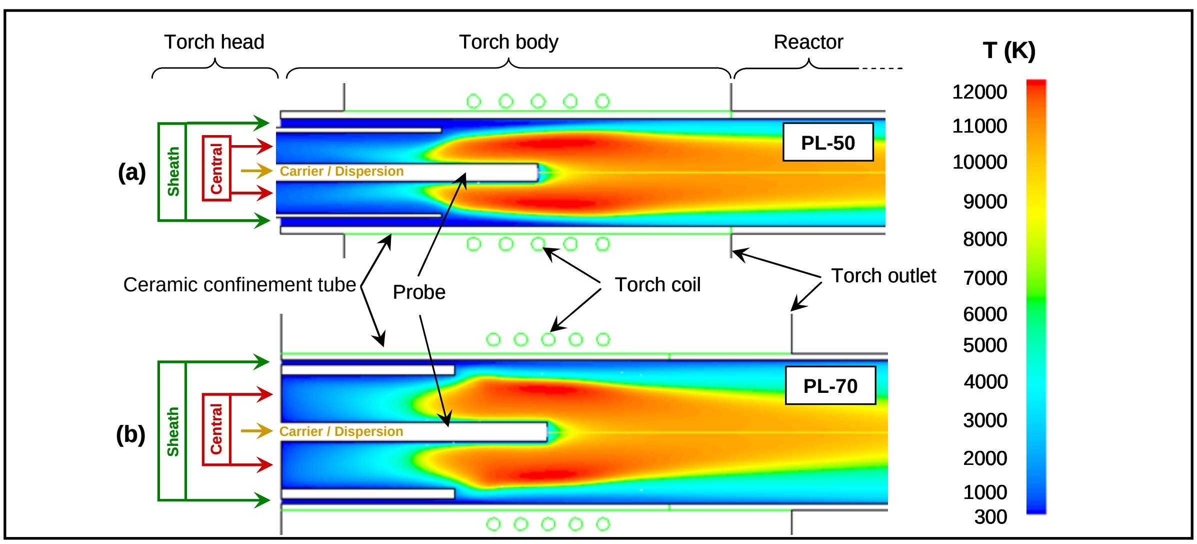

Figure 2: Modeling work showing temperature profiles in Tekna plasma torches operated under typical processing conditions. (a) PL-50 torch operating at 70 kW; reactor pressure: 4 psi; probe: 7.92 mm diameter; Torch gas composition: sheath: 120 slpm Ar + 10 slpm H_2; central: 20 slpm Ar; carrier / dispersion: none. (b) PL-70 torch operating at 100 kW; reactor pressure: 15 psi; Probe: 9.52 mm diameter; torch gas composition: sheath: 180 slpm Ar + 10 slpm H_2; central: 40 slpm Ar; carrier / dispersion: none. A temperature scale (in Kelvin) is also provided on the right hand side of the figure.

and is responsible for particles condensation as ultrafine powders with a typical mean particle size in the nanometer range (*e.g.* 10 – 100 nm). Moreover, the supersaturation of vapour species provides the driving force for particles condensation, leading to homogeneous nucleation in the gas phase. This permits the production of nanoparticles that have a rather narrow particles size distribution [4].

A wide range of nanopowders have been produced so far using the ICP technology developed by Tekna and many notable works can be found in the literature (see [5 – 9] as a non-exhaustive list). The various types of nanomaterial produced in these studies were synthesized by combining appropriately the plasma gas with the reactant injected into the torch, which can be a gas, a liquid, a solid or a liquid suspension. Other examples of nanopowders prepared with the ICP technology are presented in Figure 3. These materials have been produced at Tekna's facility as part of our R&D program using in-house plasma units dedicated to the development of new processes and new nanomaterials synthesis approaches. While R&D efforts may be required to develop nanomaterials that exhibit very specific properties, general trends can be followed to produce the required material at either small or large production rates. For instance, reducing plasmas (*e.g.* Ar/H_2) are commonly used to produce pure metallic nanopowders with oxygen-free surfaces, such as aluminum nanoparticles (Figure 3a) that are known to be extremely reactive in their non-passivated state. On the other hand, oxygen-rich plasmas (like Ar/O_2, Ar/Air and Ar/CO_2) are suitable in the synthesis of oxide nanomaterials such as TiO_2 (Figure 3b), while inert plasma are more appropriate for maintaining precursor stoechiometry. For example, B_4C nanopowders can be successfully produced under an Ar/He inert plasma using B_4C micrometric powders as reactant (Figure 3c).

The physico-chemical properties of the nanopowders can be modified through various experimental parameters specific to the ICP technology. One of the most important parameter in the nanoparticle synthesis process is the quench gas flow [7]. The quench gas flow controls the temperature of the gas stream, which in turn influences the degree of vapor super-saturation (S_v) in a gas mixture. S_v is defined as the ratio of the vapor pressure over the saturation vapor pressure at a given temperature. It is also inversely proportional to the gas temperature. In other words, when the temperature of the gas stream carrying the vapor species is sufficiently lowered, S_v exceeds a threshold value beyond which an homogeneous nucleation can occur followed by the vapor condensation in order to form solid nanoparticles. The more rapid is the change in temperature, the finer are the nanoparticles. The quenching effect on the gas stream temperature is illustrated through the modeling work presented in Figure 4. In this figure, a hot gas stream generated by an ICP torch (not shown) is flowing freely in a reactor (Figure 4a). In this case, gas cooling occurs rather slowly, essentially due to natural heat transfer phenomena.

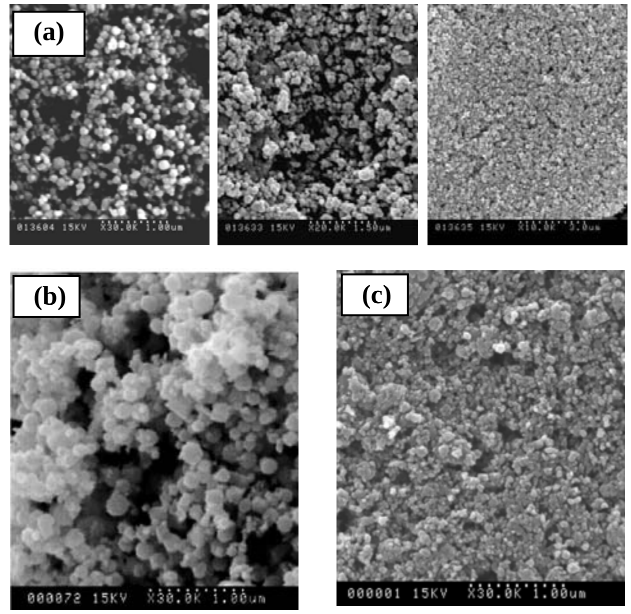

Figure 3: Typical scanning electron microscopy (SEM) images of nanoparticles prepared using Tekna's ICP technology: (a) Pure Al with tailored mean particle size (from left: 100 nm, 60 nm, 25 nm); (b) TiO_2 (mean particle size of 100 nm); (c) B_4C (mean particle size of 80 nm).

When a quench gas flow is injected radially (yellow arrows on Figure 4b), the gas temperature drops suddenly upstream. The graph in Figure 4c shows the variation of the gas temperature as a function of the axial distance along the dashed line from Figure 4b. It shows that the gas stream exits the ICP torch at a very high temperature (about 9000 K). However, as soon as the hot gas stream encounters the quench gas flow, a cold front is generated and the temperature drops drastically down to ~1000 K within an on-axis distance of less than 2 cm. In this cold front zone, the nanoparticles can nucleate and coalesce up to their final dimension. The diameter of the particles can be determined based on the following equation:

$$d_p = \frac{4\sigma_0}{\rho\left(\frac{\kappa}{m}\right)T\ln S_V} \qquad (1)$$

where σ_0 and ρ are surface tension and density of the liquid, respectively, while κ is the Boltzmann constant, m the mass of the vapor molecule and T the local temperature. Obviously, the particle size is predominantly determined by the degree of super-saturation S_v, which is inversely proportional to d_p. Such theoretical concept is supported experimentally. As an example, the influence of the quench gas flow on the mean nanoparticle size is illustrated in Figure 3a. The SEM image shows that under low quench flow conditions (Figure 3a, left), particles are relatively large in size (~100 nm). In contrast, high quench flow conditions (Figure 3a, right) limit particles coalescence after the nucleation stage, leading to nanoparticles that have a much smaller mean diameter (~25 nm).

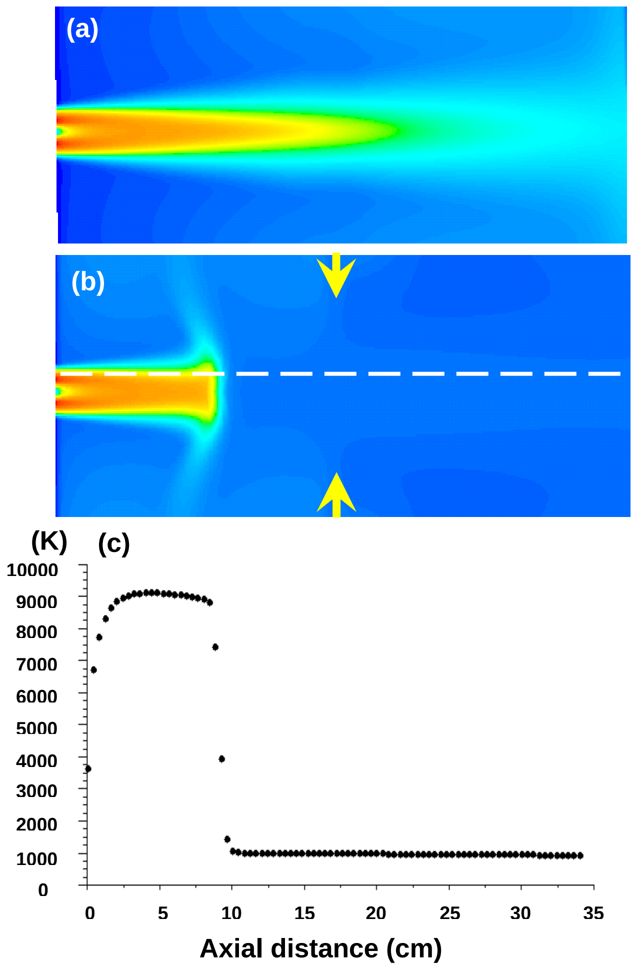

Figure 4: Influence of the quench gas flow on the gas stream temperature. (a) Temperature profile of the gas stream without quench. (b) Same conditions as in (a), but with a quench gas flow injected radially (arrows). (c) Gas temperature as a function of the axial distance identified by the dashed line in (b).

The turn-key plasma units developed and manufactured by Tekna are characterized by a high versatility and a very good reliability with appropriate robustness (allowing operation in harsh environment) as well as many fully automated functions for ease of operation. Moreover, the systems are designed to permit nanopowder synthesis in a continuous production mode. These features make the ICP technology particularly attractive in the synthesis of a wide range of nanopowders, at laboratory or industrial scales. Laboratory-scale nanopowders production requires unit with a torch power of typically 30 or 60 kW (two standard power levels commercialized by Tekna), which is normally sufficient to develop new nanomaterials and produce small batches. A typical integrated laboratory-scale (*i.e.* 60 kW) plasma unit is presented in Figure 5. On the other hand, an industrial-scale production requires higher torch power (*i.e.* 100 and 200 kW), essentially to achieve higher production rates.

Figure 5: Typical 60 kW plasma unit commercialized by Tekna for laboratory-scale nanopowders synthesis. The nanopowder produced in the reactor is carried up to the secondary filter mounted on a glove-box, allowing safe nanopowder collection and handling and packaging under inert environment without interrupting nanopowder production.

1 CONCLUSION

The ICP technology commercialized by Tekna Plasma Systems Inc. is perfectly adapted to face the growing needs in new nanopowders development at the laboratory scale or industrial-scale production. The worldwide-recognized expertise in ICP technology developed by Tekna, since its incorporation in 1990, can be utilised to design specific processes or to customize the equipments according to particular needs. By combining versatility and capability, the nanopowder synthesis units proposed by Tekna can produce safely and affordably high-quality advanced nanomaterials.

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