Quenching design for plasma synthesis of nanoparticles

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Summary

During nanoparticle synthesis by thermal plasma, the temperature encountered by the particles has an enormous influence on the final size distribution. Therefore CFD modelling has been used to predict the temperature profiles. The influence of several quenching parameters, like gas flow rates and composition, quench positions and quench jet geometries on the resulting temperature profiles have been investigated. The modelling has been supported and validated with experiments, in-situ diagnostics, and ex-situ measurements.

In this work two different quench nozzle designs, a two jets nozzle and a ring with eight nozzles, have been compared. The ring shows a better quenching behaviour at 56 slpm Ar than the two jets nozzle. A threshold amount of around 50 slpm Ar quenching gas is necessary to show a cooling effect for the ring design. With an optimised quench jet design, a high cooling rate of approximately $1 \times 10^7$ K/s could be obtained even with 56 slpm of Ar quench gas.

The combination of experiments, modelling and diagnostics is a powerful tool to optimise the plasma synthesis of nanoparticles.
Keywords

Quenching, modelling, enthalpy probe, thermal plasma, nanoparticles

1. Introduction

Nanoparticles have different properties compared to the same conventional bulk material and can therefore be regarded as different matter. These different properties occur due to the particle size being below the characteristic scale of the specific property and to a high ratio of surface to volume atoms as compared to the bulk material [1].

Depending on chemistry, size and size distribution, the nanoparticles find application in several fields: cosmetics, solid propellants, catalysts, pigments, alloying of normally immiscible solids, medical applications, quantum dots, gas sensors, high temperature super conductors, to mention just a few of them.

The synthesis of nanoparticles can be divided into the kind of nanoparticles: oxides and non-oxides or by their production techniques. Andrievsky [2] for instance, gives an overview of gas, liquid, and solid phase nanoparticle synthesis. From these three routes the gas phase one has several advantages over the liquid and solid phase routes such as product purity, continuous production, good process and product control [3].

The thermal plasma techniques [4], as being one of the gas phase routes, in particular the inductively coupled plasma (ICP) [5] process, offer many advantages over the other techniques. A high temperature and a high energy density enable the processing of high refractory materials, and the use of inexpensive available solid precursors [6]. Furthermore, the ICPs electrodeless operation results in less contamination of the products and also allows the use of aggressive gases and precursors like chlorides and oxygen.

The ICP produced nanoparticles are synthesised by a so-called vaporisation/condensation process. Due to the high plasma temperature (8000 – 10000 °K) any species, depending on its size, regardless its state, can be evaporated and/or atomised. As the plasma cools down a supersaturated vapour is formed and
condenses forming the nanoparticles. The size distribution of the particles is
determined by the temperature profiles encountered during cooling. Controlled, rapid
heat extraction, i.e. quenching, is therefore a prerequisite to tailor the particle size
distribution and offers the possibility to freeze specific thermodynamic states.

Quenching can be carried out by using for example an expansion nozzle [7], a cold
surface on which the particles condensate and can be scraped off [8], and quenching
rings / nozzles [9]. The quenching ring has some advantages over the others like for
instance: easy to position, variable quench rates, use of a reactive quench gas.
Although the quenching process is often mentioned in articles dealing with
nanoparticles synthesis, it is usually not described in much detail. Only a few
references are available on this topic. Hansen et al. [9] reported on modelling of
quench ring designs for a flame reactor. Soucy et al. [10] investigated the radial mixing
of two gas streams.

2. Experimental

Set-up

The experimental set-up of the ICP equipment is schematically drawn in Figure 1. It
consists of an induction plasma torch coupled to a modular vacuum synthesis
chamber, equipped with view ports for in-situ monitoring and in-line sampling, and a
filtration unit consisting of a main and a sampling filter.

The plasma torch (PL-35, TEKNA Plasma System Inc., Canada) uses a four turns
induction coil, a water cooled ceramic tube with a 35 mm inner diameter and another
ceramic tube with a 30 mm diameter separating the central gas from the sheath gas.
The stainless steel injection probe is water cooled and has an inner diameter of 3 mm.
It is positioned axially into the torch down to the first turn of the coil. A schematic
drawing of the torch configuration is represented in Figure 1, right.

The plasma torch is connected to a radio frequency power supply (Elgotec AG,
Switzerland) delivering an electrical power of 35 kW at a frequency of 13.56 MHz.
Figure 1: Left: schematic drawing of the experimental set-up. Right: schematic drawing of the ICP torch.

Experimental procedure

The aim of this study was to characterise the influence of quenching on the plasma properties (temperature and velocity). Therefore, a CFD code has been used to predict the temperature and velocity profiles, which has been validated experimentally using an enthalpy probe. Ar, as well as N₂, has been investigated as quenching gas for a simple two jets nozzle and an eight nozzles quench ring geometry.

Commercially available micro-sized powders were used as precursor: a d₅₀ of 1.1 micron in case of WC and 16 - 44 microns for Si. These inlet powders were fed into the torch along with the carrier gas (Figure 1) using a dense phase powder conveying system (PowderCube, DACS, Switzerland), able to transport also non- or poor-flowable powders.

All the experiments described were performed in an Ar-H₂ plasma (typically 1-10 slpm Ar for carrier gas, 6 to 27 slpm Ar for the central gas and 80 slpm Ar with 2 - 10 slpm H₂ for the sheath gas).
Characterisation methods

The local enthalpy and velocity of the plasma were determined with an enthalpy probe [11] (Tekna Plasma Systems Inc., Canada). The several view ports available on the synthesis chamber and different probe tip heights, allowed measurements at different axial positions. A moveable axis enabled measurements at different radial positions. The results were used to validate the CFD model. A mass spectrometer was linked to the enthalpy probe system to obtain information of the local plasma composition.

The in-line sampling device used in this research, based on the one used by Dobbins and Megaridis [12], consists of a rod with a sample holder at its end which can be inserted in the centre of the plasma to extract particles.

Images of the synthesised products were made using a scanning electron microscope (SEM), Zeiss, DSM 962 and a high resolution scanning electron microscopy (HR-SEM), Hitachi S4800, equipped with an EDAX/Ametek detector for energy dispersive X-ray analysis (EDX) measurements.

An X-ray Diffraktometer (Siemens D5000) operating with MoKα radiation was used for crystallographic phase characterisation.

Surface specific area (SSA) measurements, also called BET measurements, were performed using a gas adsorbing system (Micromeritics, USA), from which information on the average particle size can be obtained.

The modelling of the plasma and quenching designs, was carried out using Fluent 6.1.18, a commercial CFD software. The physical properties of the plasma gases at higher temperatures were retrieved from [13, 14]. The plasma was modelled being a simple heat source (net input 15 kW) and assumed to be incompressible sub-sonic, using a realizable $k – \varepsilon$ model. The 2D grid consisted of 40'000 quadrilateral cells. The 3D grid consisted out of 250'000 hexahedral and tetrahedral cells. In a first approximation the electromagnetic field has been neglected, since only the flow field outside the torch is investigated.
3. Results

Plasma

The left picture in Figure 2 shows the calculated temperature of the plasma outside of the torch exceeding 4000 K. The right photograph shows the plasma for the same conditions as the modelling (the plasma is assumed to be visible until the temperature drops below 4000 K, estimated from enthalpy probe measurements). The visual observation of the plasma shows a good agreement with the model.

Figure 2: Left: modelled plasma (5 slpm Ar carrier gas, 27 slpm Ar central gas, 80 slpm Ar and 6 slpm H₂ sheath gas, 40 kPa and 15 kW). Right: photograph of the plasma at the torch exit, without quenching (same conditions as the model).

Enthalpy probe measurements were carried out to characterise the plasma for various plasma compositions, power levels, pressures, and quench gas rates. The data were extracted at different axial (z = 4, 18, 60, 75, 80, and 95 mm) and radial positions, wherein z refers to the distance from the torch exit.

In Figure 3 a comparison is made between the model and the results of the enthalpy probe for the following plasma conditions: 1 slpm Ar carrier gas, 27 slpm Ar central gas, 80 slpm Ar and 2 slpm H₂ sheath gas, 40 kPa, 15 kW, 2.8 slpm Ar quenching gas (this is defined as the "no quenching" condition).
A good match is obtained between the calculated and measured temperature and velocity profiles.

**Two jets nozzle design**

A simple quenching configuration, the symmetric two jets nozzle, has been modelled and investigated experimentally. The jets are positioned in an opposite direction, have a 4 mm internal diameter, and are directed perpendicularly to the plasma. The distance between the nozzle exits amounts 108 mm, which are well outside the plasma.

The calculated results (3D), left picture in Figure 4, show a splitting of the plasma, when quenched with 56 slpm Ar at z = 75 mm. The photograph in Figure 4 shows a picture of the plasma at the torch exit as it is being quenched with 56 slpm Ar. The modelling results are confirmed by visual observations. The asymmetry of the plasma is caused by a small misalignment of the two jets. Furthermore, it should be noted that the point of view in Figure 4 is not exactly the same for both pictures.

The experimental conditions where 5 slpm Ar carrier gas, 27 slpm Ar central gas, 80 slpm Ar and 6 slpm H$_2$ sheath gas, 40 kPa, and 15 kW.
From comparison between the pictures in Figure 4 it can be said that model shows a good agreement with the experiments.

Figure 4: Left: Result of the (3D) CFD modelling at 56 slpm Ar (top is at the torch exit). The square represents the quenching ring position. Right: the plasma as observed by quenching with a two jet quench nozzle (one jet behind the plasma is not visible) at the same conditions.

Ring design

To improve the symmetry of the plasma after quenching, a ring design has been modelled and developed. Figure 5 shows a ring as being used in the experiments. It has an inner diameter of 64 mm and is composed of 8 jets, which are distributed equidistantly. Each jet has an internal diameter of 2 mm and is perpendicular to the plasma jet direction. In the axi-symmetric 2D model, the jets have been represented by a 125 µm slot. The reason for working with 2D modelling is that one is able to get good information on the process in significant less time than 3D modelling. Although it should be mentioned that the 2D model is not able to pick up 3D features caused by the single jets (see for example Figure 10), it certainly gives a good indication of what to expect.

Figure 5 shows a photograph of the plasma as quenched with 56 slpm Ar (position of quench ring z = 75 mm, 10 slpm Ar carrier gas, 27 slpm Ar central gas, 80 slpm Ar and
6 slpm H₂ sheath gas, 40 kPa, and 15 kW). The pictures in the middle and right of Figure 5 show the modelling results for quenching with 56 slpm Ar (middle) and with 120 slpm Ar (right).

Figure 5: Left: Plasma as observed by quenching by the 8 nozzle quench ring with 56 slpm Ar. Also visible in this picture are some fringes at the edge of the plasma, probably caused by plasma flowing between two subsequent jets. Middle: 2D model for same conditions. Right: 2D model for 120 slpm Ar quench gas. The squares represent the quenching position.

The 2D model shows a good agreement with the visual observations. Although the value for the quench gas flow rate is overestimated by the model, it is able to show the main features of the plasma. This overestimation is caused by representing the jets by a slot. The slot reduces the momentum of the quenching gas and thereby the penetration of the plasma, because the mass is no longer concentrated around the nozzles but over the entire ring.

Some results of the quenching ring design measured by enthalpy probe are presented in Figure 6. The curves show the enthalpy and temperature for a series of different quenching gas flow rates as a function of the radial position (0 equals plasma centre). For calculation of the temperature profiles the composition is assumed to be homogeneously mixed for all quench gas rates, although mass spectrometry measurements with nitrogen as quenching gas show that this is the case for quench rates above 56 slpm.

From Figure 6 it can be concluded that under the current ring configuration about 50 slpm of Ar and N₂ quenching gas is necessary to completely penetrate the plasma core.
Figure 6: enthalpy of the plasma at different radial positions as a function of the Ar (left) and N$_2$ (right) quench gas flow rate. Quenching position at $z = 63$ mm and measured at $z = 75$ mm. Plasma conditions: 5 slpm Ar carrier gas, 27 slpm Ar central gas, 80 slpm Ar and 6 slpm H$_2$ sheath gas, 40 kPa, and 15 kW.

**Nanoparticles**

The main focus was put on the synthesis of metals and non-oxide ceramics, since one of the advantages of the ICP process over other processes is its ability to carry out experiments in controlled atmosphere. Figure 7 shows an example of Si nanoparticles.

Figure 7: TEM picture of ICP synthesised nano silicon Si. The precursor size was ranging between 16 – 44 µm.
The influence of (non)-quenching on the resulting size of the products is shown in Figure 8. A particle growth is observed without quenching, as compared to the precursor. The non-quenched product also shows a smaller size distribution, because the vapour nucleates on the non-vaporised precursor particles. A clear reduction of the particle size is visible when quenching is being used. The size distribution depends on the temperature and velocity profiles followed by the particles.

Figure 8: Left: SEM picture of WC precursor. Middle: SEM of plasma processed WC without quenching. Right: HR-SEM picture of plasma processed WC with quenching (white bar equals 2 μm in the SEM pictures and 200 nm in the HR-SEM picture).

As already mentioned in the introduction, quenching may not only influence the particle size, but also the chemistry. The XRD spectra in Figure 9 show the phase composition of plasma processed tungsten carbide (WC, d50 of 1.1 μm) as a function of the quenching gas flow rate.

Figure 9: phase composition of ICP synthesised WC as determined with XRD for several quench gas rates of Ar (left) and for comparison between 70 slpm of Ar and N2 quench gas (right). X: WC, #: WC1-x, O: W2C, +: W.
The solid WC precursor consisted out of pure WC. The amount of WC was ~5 wt% after processing and increased to ~25 wt% after increasing the quenching gas flow rate from 2.8 to 70 slpm Ar. The remaining fraction is distributed among the sub-stoichiometric WC phases. These carbon deficit phases are formed due to the reducing atmosphere (formation of CH compounds which are no longer available for the carburisation). By adding methane to the plasma the decarburisation can be countered to obtain almost pure WC [6].

4. Discussion and conclusions

The model is able to describe the observed phenomena and therefore the CFD modelling, in combination with measuring techniques, is a powerful tool to design and optimise quenching devices, which are necessary to control size distribution and phase composition of plasma processed nano particles.

The 2D modelling is able to pick up trends as being seen from observations of the plasma, although the quench flow rate values are not exactly the same as actually used in the experimental work. This difference is caused by the nozzles being represented by a slot, which results in loss of momentum necessary to penetrate the plasma. A 3D model would describe the quenching process more exactly.

The quenching of the plasma with a quench ring is more preferable than with a simple two jets nozzle as Figure 4 and Figure 5 show. The two jets nozzle splits the plasma in two parts, without cooling the whole plasma, giving rise to strongly variable temperature and velocity profiles.

Figure 6 shows that around 50 slpm of Ar quenching gas is needed to penetrate the plasma jet (conditions: 10 slpm Ar carrier gas, 27 slpm Ar central gas, 80 slpm Ar and 10 slpm H₂, 40kPa, and 15kW). A lower quench gas flow rate does not have the momentum to penetrate the plasma and will only cool the edges of the plasma. A flow rate above 56 slpm of N₂ quenching gas is necessary to completely penetrate the plasma as can be concluded from Figure 6 and mass spectroscopy measurements.

As shown in Figure 9, quenching can also have an enormous influence on the final composition. The amount of W₂C is drastically reduced in the final composition, while
WC and W increase if the flow rate of Ar quenching gas is increased. Not only the flow rate, but also the kind of quench gas has a strong influence on the composition, therefore N₂ was used as quenching gas a well. The use of nitrogen as quenching gas favours W₂C, whereas WC is favoured when quenching with Ar.

By quenching at \( z = 63 \) mm with 56 slpm Ar, the temperature can be reduced by approximately 1500 K. The distance between the earliest available measuring point (enthalpy probe tip at \( z = 75 \)) and the quench ring position amounts 12 mm. The mean gas velocity between these positions equals approximately 90 m/s. The quenching rate is equivalent to \( 10^7 \) K/s, under these conditions. The actual value will be higher at the quenching height since the quenching takes place almost immediately.

Future work will consist out of modelling quench designs in 3D as well, to explain and show features (like for example the fringes in Figure 5) which can not be picked up in a 2D model, see Figure 10. Also the construction of a new ring having a swirl component and a plasma gas guidance system is planned.

Figure 10: cross section of a 3D model for 8 nozzle quench ring showing at \( z = 68 \) mm. The 3D model shows the presence of hot zones between the nozzles, which can not be picked up by the 2D model.
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