Plasma Synthesis of Nanoparticles

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Abstract

This paper gives a review on the plasma synthesis of nanoparticulate powders. The concept of plasma synthesis is used quite comprehensively, it covers all processes where charged particles are observed. Therefore, the topic of this paper ranges from high-temperature processes and microwave processes to the laser and flame synthesis of nanopowders. For each of the processes discussed in this paper, the product characteristics are explained. This may be used as guidance for the selection of a process. The presentation of the paper is quite basic; this is to give people working in industry on daily problems a chance to see what is going on in this field. There is a vast amount of literature in the field of plasma synthesis. The literature was therefore selected in a way to demonstrate basic phenomena and not to give a comprehensive review of the literature.

Keywords: Nanoparticles, Plasma, RF processing, Microwave Synthesis

1. Introduction

Gas-phase processes are environmentally benign as they are not connected to liquid effluents. The cleaning of liquid effluents is difficult and costly. In addition, because the synthesis of nanopowders is in most cases connected with low concentrations, the amount of solvents needed in the process is huge. Powder synthesis based on reactions in the gas phase is based on purely random processes for particle formation. In general, this leads to a broad distribution of particle sizes and, in some variants of these processes, to the formation of particle clusters. There are applications where broad particle size distributions and clustered particles are disadvantageous. To solve this problem, many process variants and nuances in processing were developed.

A broad group of gas-phase processes is connected to plasma. Generally, plasma is considered as being a distinct state of matter. It consists of positively and negatively charged elements (electrons, ions, or nanoparticles) in such a way that the sum of all electric charges is zero. These electrically charged elements are intermixed with neutral gas atoms or molecules. The degree of ionization, which is the ratio of charged particles over the uncharged ones, may be quite small. Due to the mobile electric charges, a plasma is electrically conductive. A plasma containing particle is called dusty plasma. Particle synthesis is always connected to dusty plasma. In addition, one has to ask for the thermal equilibrium in the plasma, which is a further important point for the classification of plasma processes. One distinguishes between equilibrium plasma and non-equilibrium plasma. In the first case, the thermal energy (may be represented as temperature) of all constituents is equal. This is also called thermal plasma. In the non-equilibrium case, the different constituents of the plasma have different thermal energy levels. In this case, the electrons have the highest, the ions a significantly lesser, and neutral gas species the least energy. It is important to note that any flame is partially ionized; therefore, it is often called low-temperature partial plasma. This is an interesting point waiting for final exploitation.

Within the large group of plasma processes for
nanoparticle synthesis, a very special class of methods is connected to plasma produced by electrical systems. The other processes where plasma is involved apply laser or just high temperatures for excitation. One additional characteristic to differentiate plasma processes is the gas pressure. Some of the processes work at ambient pressure, however, most of them at reduced gas pressure. A third means to differentiate plasma processes is based on the precursors. They may be gaseous, solid, liquid, or solutions.

2. High-Temperature Plasma Processes

2.1 AC and DC systems

High-temperature plasma processes are the oldest and most common ones. They work at atmospheric pressure and use electric power originating from DC, AC, or RF sources. In high-temperature plasma processes, the energy distribution is usually close to thermal equilibrium. Fig. 1 shows two distinct types of arrangements applied for powder synthesis using AC or DC electrical power. In both cases, the plasma burns between two co-axial electrodes. It is blown out of the system by a powerful gas stream. This gas stream fulfills two major tasks: It is the gas supply for the plasma and it prevents the electrodes from overheating. An additional water-cooling system may be necessary in the case of high-power systems. Reactive components such as oxygen or ammonia necessary to obtain the intended product from the selected precursor may be admixed. The two arrangements for plasma synthesis depicted in Fig. 1 differ in the supply of the precursor. Systems such as those may use solid precursors supplied as powder or liquid precursors supplied in most cases as an aqueous or organic solution. In the latter cases, the energy content of the plasma flame is influenced dramatically.

In the case of axial feed of the precursor, the precursor is sucked into the system by the co-axial gas stream. Generally, the designs provide a sheath gas circumferentially to the nozzle system to avoid unplanned deposition of the product on the structures of the system. In most cases, an additional pump for the precursor is not necessary. Feeding the precursor from the side directly into the plasma flame is, at most, applied for powders only. The temperature in the plasma is extremely high. One may expect temperatures significantly above 4000 K. At this temperature, all of the metals and most of the oxides are already evaporated, or at least melted. Therefore, as the precursor largely evaporates, one has almost no problems with respect to particle or droplet size. In this instant and in the case of applying an RF plasma, the design of the nozzle is the crucial point with respect to the processing parameter. Nozzle design ranges from very simple ones to highly sophisticated ones with hypersonic gas velocities 1,2.

Within the plasma, the particles move in the direction of the gas stream, and in addition, they move randomly. Just as in any other aerosol process, there is therefore a high chance for particle collision and the formation of clusters. The probability of cluster formation is reduced significantly by the rapid cooling of the gas immediately after the reaction zone. The design of this quenching zone is crucial for the product quality. The quenching gas is introduced into the system either radially or axially against the flow direction. Quenching improves the quality of the product. In the context of nanopowders, improving means narrowing of the particle size distribution and avoiding large particles or agglomerates. For many applications, a reduction of the average particle size is seen as an improvement of the quality.

Fig. 2 shows the typical flow diagram of a production system for powders using a plasma torch system at ambient pressure. After synthesis, a quenching step follows. Furthermore, it may be important to recirculate the process gas. Examples where this is necessary are, e.g. the synthesis of nitrides, where pure nitrogen or nitrogen/ammonia mixtures are used for nitriding and in the case of metal carbide synthesis, argon is used as the carrier gas in most
cases.

Even when it is not always a disadvantage, processes using AC or DC plasma torches suffer from the prejudice of producing only highly agglomerated powders. A typical example for such a product is depicted in Fig. 3. This figure depicts aluminum nitride, AlN. Aluminum nitride is a highly hygroscopic ceramic with excellent electric insulating properties. It is extremely difficult to synthesize nanoparticulate AlN. In this instance, AlN was synthesized from aluminum vapor in a 50/50 vol% nitrogen/ammonia atmosphere. An ablating aluminum electrode was used as the source for the metal vapor. To obtain sufficiently high plasma temperatures, the plasma was supplied with electrical energy using a pulsed DC source. The nozzle was designed in a way to obtain hypersonic gas velocities.

Two characteristic features characterize the product shown in Fig. 3: There is quite a broad particle size distribution. It is interesting to see that the smaller particles are arranged in chains. The diameter ratio between the largest to smallest particles seems to be in the range of ten. The particles, in particular the largest ones, are not spherical. By careful selection of the processing conditions and the precursor, it is also possible to obtain a product with spherical particles and a relatively narrow particle size distribution. As an example, Fig. 4 shows an electron micrograph of zirconia powder.

Karthikeyan et al. used a 2.4-wt.% zirconia solution made of zirconium butoxide dissolved in n-butanol. This liquid was injected radially into the plasma torch. The transmission electron micrograph shown in Fig. 4 is characterized by almost spherical particles with an average particle size of around 12 nm. Besides the majority of particles of nearly equal size, a few huge particles with a diameter of around 45 nm are visible. The electron diffraction pattern inserted into Fig. 4 represents these visual findings perfectly. It shows the diffraction rings stemming from the tetragonal small particle fraction and, additionally, a few separated spots originated from the few large particles. These larger particles were crystallized in the monoclinic structure. In general, one can say that
the product shown in Fig. 4 is almost perfect.

Plasma synthesis using AC or DC power sources is a mature and widely used process that led to a vast amount of literature where, however, the most important technical details are kept secret because of their huge technological relevance. Some interesting recent results may be found in 4-9.

2.2 RF systems

Fig. 5 shows the typical layout for an RF plasma device for nanopowder synthesis. It consists of a system to introduce process gas and precursor. This part of the system is set up similarly to the one for plasma processes using DC or AC power. The frequencies applied in such systems range from 50 kHz up to 10 MHz.

The only and important difference is the fact that these RF systems work without electrodes. There is therefore no risk of contamination from the electrodes, and in addition, these systems do not have any wear parts with a limited service life. On the other hand, consumable electrodes cannot be used as precursors. Besides the design shown in Fig. 5, a design where the flow of the precursors is opposite to the streaming direction of the plasma flame is also described. It is said that such a design has the advantage of a longer time period where the product is in direct contact with the hot plasma flame 10,11. This may be of advantage in the case of products where the reaction rate of particle formation is extremely low.

Moreover in inductively coupled RF systems, quenching improves the quality of the product, narrows the particle size distribution and avoids large particles. As an example, the comparison of silica powders produced with identical production parameters except for quenching is shown in Fig. 6a and 6b 12. The powder shown in the electron micrographs
in Fig. 6a was produced without quenching. At the first glance, the most characteristic features of the unquenched product are a few huge spherical particles surrounded by many smaller ones, visibly a broad particle size distribution. This is different in Fig. 6b, where the product obtained after quenching is shown. (The magnification in Fig. 6b is more than double that of Fig. 6a) In this product, the huge spherical particles are missing. Certainly, the particle size distribution remains broad, however, the tail on the large particle side of the size distribution is not that significant.

Complete systems in accordance with those shown in Fig. 1 and 5 for industrial powder production are commercially available. A typical plant is shown in Fig. 7. The production capacity of synthesis plants like this is in the range of kilograms per hour.

Optimized industrial production systems deliver nanopowders of sufficiently good quality with particle sizes of less than 100 nm. The range of possible products is broad; it ranges from metals and oxides to carbides and nitrides. Except for the oxides and the powders of precious metals, all of these products may indeed be highly pyrophoric. It is therefore advisable to handle these products in an inert gas atmosphere, if possible within glove boxes. A typical example of such a nanopowder is shown in Fig. 8. This figure shows copper powder produced with equipment such as that shown in Fig. 7.

The product shown in Fig. 8 has a particle size distribution that is not too broad. With respect to the fact that this is a product of commercial and not laboratory equipment, the size distribution is remarkably good.

A few further more recent applications of powder synthesis applying RF plasma torches outside of industrial use are found in. It may be interesting to realize that high-temperature plasma applications are perhaps driven with microwave power sources, too.

3. Low-Temperature Plasma Processes

3.1 General considerations

Low-temperature plasma processes are always connected to systems with reduced pressure. In this context, low-temperature systems may be defined as ones that apply temperatures below 1000 K. In these systems, the power is introduced either by RF or microwave power supplies. Even if that appears almost identical, the physics of using RF or microwaves is to some extent different. To understand the influence of the frequency, one has to study the energy transfer to charged particles in an oscillating electrical field. The energy $U$ transferred to a particle with the electric charge $Q$ in an electrical field with the frequency $f$ is inversely proportional to the mass of the particle $m$ and the squared frequency.

$$U \propto \frac{Q}{mf^2}$$

As the mass of the electrons is a few thousand times smaller than the mass of the ions, a few thousand-fold
larger amount of energy is transferred to the electrons, as compared to the energy transferred to the ions. In addition, an RF system works with frequencies up to the megahertz range; microwave systems are in the gigahertz range. Therefore, in a microwave system, there is six orders of magnitude less energy transferred to the charged particles as compared to an RF system. This favors low-temperature systems. In both cases, the plasma is not in thermal equilibrium; the “temperature” of the electrons is significantly higher than that of the ions or neutral particles. The “reaction temperature” is therefore an average value determined at the exit of the plasma zone.

Equation (1) is valid for one isolated charged particle in an oscillating electrical field only. The situation is different in a plasma, there, one finds free electrons, ions, dissociated gas and precursor molecules in addition to neutral gas species. Therefore, collisions between charged and uncharged particles limit the mean free path of the charged particles accelerated in the electric field. This influences the energy transfer to the particles. The collision frequency \( z \) of the gas species must therefore be considered\(^{20} \). This changes equation (1) to:

\[
U \propto \frac{Q}{m} \frac{z}{f^2 + z^2} \tag{2}
\]

Equation (2) shows the reduction of the energy transfer to the charged particles by collision with other neutral species. The collision frequency \( z \) in the plasma depends on the gas pressure. As a rule of thumb, one can say: In a RF system, \( z \) is significantly larger than \( f \); whereas in microwave systems, \( z \) and \( f \) are almost equal, usually, the gas pressure is adjusted such that the microwave frequency is larger than the collision frequency. This makes a significant difference. In RF systems, because of the short free path length of the electrons, the energy of the electrons is in the range of a few eV, whereas the energy of electrons in a microwave plasma is in the range of keV. Electrons with energies of just a few eV can attach to the surface of particles; this is different in the case of energy rich electrons, as they ionize the particles. Therefore, in RF systems, one expects negatively charged particles, whereas the electric charge of particles in microwave systems is positive. In both cases, in good approximation, the electric charge of the particles increases linearly with the particle diameter\(^{20} \).

**Fig. 9** shows the charge of nanoparticles in an RF electrical field as a function of the diameter\(^{21} \).

The increasing charging of the particles with increasing diameter has severe consequences on the processes of particle coagulation and agglomeration. Particles with electric charges of equal sign repel each other. As the charge of the particles increases with increasing particle diameter, particles with larger diameters repel each other more than ones with smaller diameters. This suppresses the formation of larger particles and the formation of agglomerates.

**Fig. 9** Average number of electric charges carried by a single nanoparticle. The particle charge increases linearly with the diameter over many orders of magnitude.\(^{21} \) Reproduced by permission of Springer.
In other words: In a well-designed low-temperature plasma system for the synthesis of nanoparticles, one obtains particles with a narrow particle size spectrum.

3.2 RF Systems

As the energy transfer to the electrons is quite good, it is necessary to operate at relatively low gas pressures to avoid too high temperatures. Usually, the gas pressure is selected to be in the range between 0.1 and 1 mbar. Such a low gas pressure limits the production rates significantly. These processes are therefore only used to synthesize small quantities of highly specialized materials. A typical system using a capacitive-coupled plasma according to Anderson et al. is shown in Fig. 10.

The designers of the equipment shown in Fig. 10 claim that besides simple oxides, such a device allows the synthesis of complex oxides such as high-temperature superconductors and nitrides. Generally, the synthesis of metal powders should be possible, too, provided that one finds a possibility to avoid condensation of the product on the walls of the reaction tube.

Well-suited for the synthesis of metal powders is the RF system shown in Fig. 11. By abandoning the advantage of an electrodeless system, the designers of the device shown in Fig. 11 achieved a series of additional advantages. However, in this case also, the design is for small production quantities.

The design of Matsui works with a pulsed RF plasma. The pulse length is in the range up to 30s. As an example, the authors show the synthesis of FePt, a hard magnetic intermetallic compound. For both constituents, organic compounds were used as precursors. There was a steady flow of gas through the reaction zone, which is the space between two permeable electrodes. As long as RF power was on, the particles stayed in the reaction zone and grew. After switching off RF power, the particles moved out of the reaction zone and were collected. Therefore, with increasing pulse duration, the particle size increased. This behavior is shown in Fig. 12.

As the charge of the particles increased with increasing pulse time, coagulation and agglomeration of the particles was almost impossible. Therefore, for each pulse duration, a certain equilibrium particle size may be expected. Indeed, electron micrographs show that the particles are in a very narrow range of sizes. A typical electron micrograph of such a product is shown in Fig. 13.

This electron micrograph shows that all particles are of equal size. This batch was produced with a plasma-on time duration of 5s. The particles with a diameter in the range between 30 and 35 nm are almost spherical. The average size was about 33 nm and the
size variation was within \( \pm 12\% \).

3.3 Microwave systems

3.3.1 Microwave processes working under reduced pressure

A low-pressure microwave system promises the lowest reaction temperatures. One may therefore expect the least agglomerated product. And in fact, by an appropriate design of such a system, these promises can be fulfilled. Vollath succeeded as the first one to design such a system. It is shown in Fig. 14.

A long reaction tube that passes through a tuned microwave cavity characterizes this design. At the intersection between reaction tube and cavity, the plasma is ignited\(^{22,25}\). The evaporated precursors are transported with a carrier gas into the reaction zone. For the synthesis of oxides, oxygen is added to the carrier gas, and for nitrides it is ammonia. A typical oxide, ZrO\(_2\), produced with such a system is shown in Fig. 15a. The product shown in Fig. 15a excels in a small variability of the grain size, an observation which is typical for this microwave plasma process. As mentioned in 3.1, in a low-pressure plasma process, the particles carry positive electric charges. One can prove this statement simply by adding water to the carrier gas. In this case, some of the water molecules dissociate and react with the particles: The positively charged particles are neutralized by collision with OH\(^{-}\) ions by the following process:

\[
H_2O \Rightarrow H^+ + (OH)^- \\
n \text{particle}^{**} + n(OH)^- \Rightarrow (\text{particle}^{**} + n(OH)^-)_{\text{neutral}}
\]

The neutralized particles carry a hydroxide layer at the surface. Besides this, as the particles are no longer repelling each other, one may expect larger particles with broad size distributions. In fact, exactly this behavior was observed experimentally. Fig. 15b demonstrates the outcome of this process. Fig. 15a shows the product with a narrow particle size distribution synthesized without water addition, whereas the product obtained after water addition is shown in Fig. 15b. What a difference! The product synthesized without the additions of water shows a grain size of around 8 nm. Most of the grains are of equal size, whereas the material produced with water additions is characterized by a broad distribution of particle sizes in the range from 10 to 50 nm. This dramatic difference between these two batches of the same material clearly demonstrated the validity of this simple model. It moreover proves that the particles are, in contrast to low-pressure RF processes, positively charged.
Zirconia is an example of a product with good crystallization properties. Many other products such as alumina, silica, etc. crystallize only poorly. In some cases, they form loose “cloudy” aggregates and not well-defined particles. Well-defined particles of alumina or silica are obtained only with high-temperature processes. On the other hand, such cloudy aggregates exhibit huge surfaces giving sometimes entirely new or significantly improved properties to the material. Fig. 16 shows such a product.

Further products in the range of the possibilities of the low-pressure plasma process are nitrides, sulfides, selenides, etc. As an example, Fig. 17 shows nanoparticulate zirconium nitride.

Fig. 17 highlights that the size-limiting phenomenon also works in the case of nitrides. In this example, the nitride was prepared from a reaction of the chloride with ammonia. Shimada et al. synthesized GaN successfully in a system using a resonant microwave cavity of different design with similar good success.

3.3.2 Synthesis of coated nanoparticles

There are additional possibilities to exploit the repelling phenomenon between the particles. The most attractive one is coating with a second phase. This second phase may be a ceramic or a polymer one. Coated nanoparticles are of special interest with respect to their physical properties. On the one hand, a coating acts as a spacer to reduce interaction of the particles, a property which is important, e.g. for magnetic particles, and on the other hand, coated particles allow the combination of different properties in...
one particle. A typical example is the combination of ferromagnetism and luminescence.

**Fig. 18** shows the set-up to synthesize coated nanoparticles in a one-pass through process. The layout shown in the figure is for one coating; however, there is no serious problem in making two or even more coatings.

The device shown in **Fig. 18** consists of two independent reaction zones connected by the reaction tube. The particles synthesized in the first reaction step act as a condensation seed in the second reaction zone. To avoid loss of the particle charges, it is important that the two reaction zones are as close as possible. Otherwise the particles will start to agglomerate before they are coated. However, for reasons of safety, it is not possible to bring the two reaction zones directly together, because at the end of each microwave cavity, a cut-off tube is needed to avoid microwave leakage. It is quite difficult to find a good compromise between microwave leakage and loss of particle charges. Replacing the second microwave cavity by a tubular furnace permits coating the particles with a polymer instead of a second ceramic phase. **Fig. 19** shows such a system.

Typical examples of coated nanoparticles are shown in **Fig. 20a** and **20b**. In **Fig. 20a**, a zirconia particle coated with alumina is shown. Please note the continuous coating of equal thickness around the particle. The same is visible in **Fig. 20b** which shows iron oxide particles coated with PMMA.

### 3.3.3 Microwave plasma processes working under ambient pressure

It was often tried to perform the process explained above at atmospheric pressure or with other simplifications. Typical designs are close to the one depicted in **Fig. 21**.

This kind of systems generates a plasma torch. The precursors are introduced after the plasma torch; therefore, the reaction zone is at a reduced temperature. However, as these systems work at atmospheric pressure, the mean free path length of the electrons is that small that within the reaction zone, number and energy of the remaining electrons is small. Therefore, particle charging and repulsion are poor. However, this design gives the chance to add downstream a second precursor to coat the particles synthesized in the first step. Additionally, the reaction temperature may be adjusted by varying the distance between plasma torch and precursor input.
Comparing these products with those obtained by the low-pressure microwave process, the qualities of the products were not really satisfying. However, this may be wrong comparison. The competing products are those produced by RF processes. This comparison shows a competitive product.

Like in many other cases working at ambient pressure, the products of this plasma process are agglomerated with broad particle size distribution. **Fig. 22** shows silver particles produced by such an equipment.\(^{32}\)

The powder shown in **Fig. 22** shows a broad spectrum of particle sizes. They range from fine fuzz to large faceted particles with diameter up to nearly 40 nm. As mentioned above, by using two consecutive supplies for the precursor, it is possible to produce coated particles, too. **Fig. 23a** shows pure cobalt powder and in **Fig. 23b** the same product, however coated with SiC.\(^{32}\)

Again, as it is characteristic for this type of processes, the particles show a broad size distribution. Additionally, these electron micrographs make clear that the particles are agglomerated; they are sintered together. Certainly, after coating these problems are not eliminated, in contrast, they got to be more severe. The differences in contrast visible in **Fig. 23b** show clearly the Co cores and the SiC coating.

### 4. Further Plasma Processes

#### 4.1 Laser processes

In general, plasma processes driven by lasers may be subdivided into two groups:

- Laser ablation processes working with solid targets and
laser processes working with gaseous targets. These processes have in common that the beam of a laser is focused to a spot. The intensity in the focus is so high that the gas phase is ionized; plasma is formed and responsible for the further progress of the reaction leading to particle synthesis. Also for these processes a wealth of literature exists, however, it is possible to extract a few characteristic design features.

Fig. 24 shows the general layout of a synthesis device according to the laser ablation process.

In the laser ablation process, a high intensity laser beam is focused onto the surface of a target. The target may be a pure metal or oxide, or even a mixed system. Because of the high-energy input coming from the pulsed laser, the material of the target is vaporized instantaneously. This process preserves even the stoichiometry of a complex mixed target in the vapor phase. The intense electrical field of the laser beam ionizes the vapor; a supersonic jet of evaporated material, a plume, is ejected perpendicular to the surface of the target. The temperature in the plume reaches values of 3800 K and more. During the adiabatic expansion of the plume, the temperature decreases and, as the vapor gets supersaturated, particles are nucleated. Within the short time interval of supersaturation, the particles are formed. The lower the gas pressure in the system, the faster expands the plume; the shorter is the time for particle formation. This limits particle growth. However, with
increasing supersaturation, the number of nuclei increases, a process that leads to small particles, too. In reality, one observes a complicated interaction between these two mechanisms. Experimental results on the dependency of the particle size as function of the gas pressure are shown in Fig. 25.

It is remarkable to see that one obtains the smallest crystallites at low and at high pressure; in the intermediate range one finds the largest particles. However, this is just half of story. Due to the high particle density in the expanding plume, there is a high probability that the particles form agglomerates. The probability of cluster formation is highest at high gas pressure, a finding that is well understood by the high particle density in the plume. By proper selection of the process parameters, agglomeration can be controlled to some extent. Fig. 26 shows as a typical example Fe₂O₃ synthesized by this process.

In this figure, one additional problem of the laser ablation process, which is typical for all gas phase processes working with high particle densities, is visible: The particle size distribution is very broad.

The second plasma process, driven by a laser, works with a gas target. A typical design is shown in Fig. 27.

It is typical for successful designs of laser gas phase synthesis that the focus of the laser is directly above the orifice, where the gaseous precursor and the reaction gas enter, already premixed, the reaction vessel. At this point plasma is formed. In the laser focus, similar as in the laser ablation process, the concentration of reactants is extremely high. Therefore, also this process suffers from the tendency to form agglomerates. Fig. 26 shows as a typical example Fe₂O₃ synthesized from iron carbonyl, Fe(CO)₅.

The product depicted in Fig. 28 shows the typical chain-shaped agglomerates which are characteristic for these processes. This micrograph shows clearly that the particles are sintered together.

Often, the absorption of optical energy by the precursor or the carrier gas is not sufficient. In these cases, the addition of sensitizer gases that have a high degree of absorption in the wavelength range of the laser, is helpful. Because of its wide availability,
the application of CO₂ lasers emitting in the infrared field is very common. However, the absorption of the 10.6-μm emission is, in general, very poor. Therefore, the addition of SF₆, which is a perfect absorber especially for this type of radiation, is widely used.

Additions of ethylene, C₂H₂, are also described. This measure, naturally, does not have only advantages. A typical example of an adverse by-effect was reported by He et al. For the synthesis of nickel nanopowders from the carbonyl, these authors added SF₆ to improve optical absorption. In the reaction product, besides the intended nickel particles, NiF₂ was detected. However, these unavoidable side reactions may be used to obtain very special products. In an experiment using Fe(CO)₅ as a precursor, C₂H₂ as a carrier gas and SF₆ as a sensitizer, David et al. synthesized α-Fe particles embedded in graphite. The carbon used for the embedding graphite stemmed from the C₂H₂, dissociated in the laser plasma. Although the reaction rate and particle density in the plasma are high, the resulting product did not lead to coated particles as they are obtained in the microwave plasma process.

4.2 Flame processes

As mentioned in the introduction, flames may be considered as “partial plasmas”, however, until now, there is only one attempt to exploit this property. The plasma properties of flames are utilized in the combination with electrical fields. This may be a microwave field to introduce more energy or a DC field to separate electrical charges according to their sign. Pratsinis and co-workers studied the latter possibility. One of the possible configurations is shown in Fig. 29a. It shows a flame emerging from a system of orifices, which can be similar to the ones depicted in Fig. 1, located between two plate electrodes. Fig. 29b shows this arrangement in operation. The electrical field strength was below 2 kV cm⁻¹. With increasing strength of the electric field, this arrangement leads to a significant reduction of the particle size. It was found that the width of particle size distribution reduces with increasing electrical field strength. The important point, visible in Fig. 29b, is that powder is collected at the surface of both electrodes.

Analyzing the experiments as shown in Fig. 29,

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Fig. 28 Iron oxide, Fe₂O₃ ex Fe(CO)₅, synthesized in a system according to Fig. 27. In this electron micrograph, it is clearly visible that the particles are sintered together in chains. Reproduced by permission of Elsevier.

Fig. 29 Set-up to synthesize nanoparticulate powders in flames connected to transversal electric fields between plate electrodes.

a Experimental set-up.

b Appearance of a flame producing TiO₂ ex TiCl₄ in a methane-oxygen flame with transversal electrical field. The electric field broadens and splits the flame. Particles charged electrically with different sign are attracted by the plate electrodes and deposited.
the most important observation is that the field strength of less than 2 kVcm$^{-1}$ is by far not sufficient to ionize the gas molecules or the particles. However, the temperatures of around 2500 K in the flame lead to thermal ionization of gas molecules or particles; even ionization of the particles with free electrons accelerated in the electric field is conceivable. Therefore there is a high probability that the particles carry electric charges. Because of the atmospheric pressure of the system, the energy of most of the free electrons is small. Therefore, the attachment of free electrons to the surface of uncharged particles is also possible. These processes lead to particles carrying electric charges of both signs that are separated in the electric field and which move in the direction of the different electrodes. As a result, the probability for agglomeration is reduced. Experimental results confirm these predictions perfectly. As Fig. 29b shows, the electrically charged particles are pulled out of the flame and are deposited at the surface of the electrodes. The almost equal thickness of the particles at the electrode plates indicates an equilibrium of the electrically charged particles in the flame$^{41,42}$.

Fig. 30a and 30b compare the products synthesized under identical conditions except for an electrical field between plate electrodes. The result is striking. Without an electrical field, the particles are found to be in a size range between 10 and 40 nm; the application of an electrical field of 1.6 kVcm$^{-1}$ reduces the particle size to a range between 5 and 10 nm. A remarkable result!

5. Conclusions

It has been shown that there is a wide variety of plasma processes that are well-suited for the synthesis of nanoparticulate powders. One may subdivide these processes into two groups:

- To produce larger quantities of powders where uniformity of the particle size distribution is not that important, plasma processes at atmospheric pressure are well suited. The plasma may be energized either with RF or microwave generators. Nowadays, both types of systems are fully developed and engineered. The development in electronic systems at least in the power range up to a few kilowatt made microwave systems cheaper as compared to RF systems. Furthermore, the design of microwave systems is significantly simpler than that of RF systems.

- To obtain highly specialized products, low-pressure microwave processes are unrivalled. Over and above this, this process also allows the synthesis of coated particles. However, it may be problematic to produce particles with good electric conductivity.

The analysis of the literature revealed that products stemming from laser processes were not accorded any importance, neither in science nor in technology.

Plasma processes combining flames with electric fields may have a high potential for further development, especially since they may be well-suited to the production of larger quantities of good quality.
References

13) http://www.tekna.com/
Author’s short biography

Dieter Vollath

Dieter Vollath, head of NanoConsulting, is since more than 15 years engaged in the field of nanomaterials. After working twelve years in the field of nanomaterials at Forschungszentrum Karlsruhe, Germany, in 2003, he founded NanoConsulting (www.nanoconsulting.de). At Forschungszentrum Karlsruhe, his activities were primarily in the field of synthesis, properties, and application of ceramic nanoparticles. With respect to synthesis, he developed the microwave plasma process, the only gas phase route for synthesis that applicable for synthesis of coated nanoparticles. In the field of properties, optical and magnetic properties were in the foreground.

NanoConsulting is devoted to help small and medium sized companies, to step into this new technology or to apply nanomaterials in their products. NanoConsulting is also engaged in education in the field of nanomaterials. Within this business area, NanoConsulting organizes courses that are specific for different companies or which are for open for any attendees. In parallel, Dieter Vollath is professor at the University of Technology in Graz, Austria. Within these obligations, he gives courses on “Ceramic Materials” and “Nanomaterials”. Dieter Vollath wrote a textbook on nanomaterials that appeared in January 2008 at WILEY-VCH.