

***FUNDAMENTALS OF THE NHALO PROCESS***

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## 1. Prologue

Atomic clusters (clusters for short) are aggregates of atoms and/or molecules in the size range from a few to million of the components. The structural and electronic properties of clusters may be very different from the solids they can eventually grow into. Their physical and chemical properties depend on the number of their components and change as the cluster size increases. How does a cluster grow step by step from molecules and how structures and properties change as the cluster grows? How many atoms are required to form a solid<sup>1</sup>?

Clusters may be divided into three size ranges: microclusters, small particles and microcrystals. These size ranges are artificial because there is no clear demarcation between the regions and different properties concerned may fall in different size regions even in the case of aggregates with same compositions. However, the table provides one view on the topic – and shows that even in the *practical nanomaterial area* of 10...100nm, the properties of the materials are size-dependent.

Table 1-I Characteristics of metal atomic aggregates with various sizes

| Clarification            | Microclusters  | Small particles   | Microcrystals   |
|--------------------------|--|---|---|
| Number of atoms          | $10^2 - 10^3$  | $10^4 - 10^5$   | $>10^6$   |
| Radius (nm)              | $\sim 1$   | $\sim 10$   | $< 50$  |
| $N_v/N_s$                | 0,1 – 1  | 1 – 10  | $< 10$  |
| Atomic arrangement       | Atomic arrangement of both inside and surface atoms have different behaviours compared with those in bulk. | Inside atoms are arranged same as in the bulk but surface shows different structure.                          | They have the same configurations as those for bulk but polarization exists on the surface. |
| Electronic properties    | Valence electrons exhibit shell structure with magic numbers.  | Quantum size effect and macroscopic quantum tunneling effect.   | Surface, plasma excitation, non-localization.   |
| Theoretical descriptions | Quantum mechanical treatment and coupling effect.  | Statistical treatment of the distribution of electronic energy levels, modified by surface correlated effect. | Solid-state energy band theory, mesoscopic theory.  |

Nanomaterials are an active field of research in many laboratories. Techniques used for nanoparticle and nanophase material synthesis include vapour deposition, mechanical milling, laser ablation, flame synthesis, sol-gel, and RF and microwave plasma synthesis. Aerosol processes for nanoparticle and nanophase material synthesis produce in general pure materials with well controlled characteristics. However, many nanomaterial processing techniques suffer from low production rates. Moreover, vapour deposition and laser ablation processes require special equipment such as ultra-high vacuum systems and high power lasers. The sol-gel process requires costly precursor chemicals. In addition, a number of the processes are material-specific and non-versatile.

Combustion flame processing of materials offers advantages such as low-cost, single-step processing, versatility and high production/processing rates. Combustion flames have been widely used for material synthesis and processing in both research and industry. Combustion synthesis has been used to produce pure metals, alloys and ceramics using both solid and gas phase reaction routes. Flame synthesis has also been used to produce oxide and multicomponent oxide powders<sup>2</sup>.

A novel technique that combines flame synthesis and flame spray processing into a single process was developed in Finland in 1990's. This technology, originally called Liquid Flame Spraying (LFS) is the background of Beneq's nHalo (Hot Aerosol Layering Operation) technology.

This training package describes the fundamentals of the patented aerosol material production technology and the deposition of nHalo-produced particles on the substrate.

## 2. nHalo process steps

Hot Aerosol Layering Operation (nHalo) is based on the combustion of gaseous and atomised liquid raw materials in an atmospheric oxy-fuel flame. This evaporation condensation controlled method produces metal oxides, noble metal nanoparticles and combinations thereof. The flexibility in the raw material feed allows for great freedom of incorporating materials with very different vapour pressures.

The basic idea of the nHalo process can be considered to be one where all the reactants required in the preparation of nanoparticles are first brought to a vaporous form, *i.e.* gas phase. Condensation of reduced components from the gas phase to a solid phase occurs extremely rapidly in such a manner, that all components contained in the reactants and required in forming the nanoparticles are brought simultaneously to a supersaturated state, in which case the composition of solid particles is very homogeneous.

In the nHalo process the nanoparticles are born *in situ* and can be immediately deposited on a substrate by the gas flow. This enables the unique feature of being able to deposit nonaggregated nanoparticles directly on a substrate.

Because the nHalo process can produce various metal oxides, multicomponent oxides, nanostructured noble metals and combinations thereof, it opens up totally new possibilities for the production of doped nanostructured coatings. Currently these coatings can be used for glass colouring and for producing hydrophilic, low-emissivity and easy-cleaning coatings. However, various other materials have been produced (in powder form) by the nHalo process and can be immediately used in coating applications, too.

The nHalo process includes the following process steps, which will be discussed in detail below.

- precursor/feedstock preparation

- atomization
- reactions in the gas phase (in the flame)
- particle interaction
- particle deposition

## 2.1. Precursor/feedstock preparation

nHalo process uses liquid raw materials and in this respect it has a close resemblance to spray pyrolysis. Spray pyrolysis is used to produce powder materials from atomized liquid precursors. Although the term spray pyrolysis is used rather loosely in the literature, it can be defined as 'powder production without added oxygen'.

The beauty with liquid raw materials is in the fact that most elements have a compound which can be dissolved to some solvent. Typically the *solvent* can be non-expensive, such as water or alcohol. The *solute* is typically a metallic salt, i.e. solid material.

It is important that the raw materials used in the nHalo process are real solutions (and not e.g. dispersions). Thus the liquid raw materials need to fulfil i.e. the following characteristics:

- i. The particles of solute are the size of individual small molecules or individual small ions. One nanometer is about the maximum diameter for a solute particle.
- ii. The mixture does not separate on standing. In a gravity environment the solution will not come apart due to any difference in density of the materials in the solution.
- iii. The mixture does not separate by common fiber filter. The entire solution will pass through the filter.
- iv. Once it is completely mixed, the mixture is *homogeneous*. If you take a sample of the solution from any point in the solution, the proportions of the materials will be the same.

- v. The mixture appears clear rather than cloudy. It may have some color to it, but it seems to be transparent otherwise. Light is not scattered by the solution. If you shine a light into the solution, the pathway of the light through the solution is not revealed to an observer out of the pathway.
- vi. The solute is completely dissolved into the solvent up to a point characteristic of the solvent, solute, and temperature. At a *saturation point* the solvent no longer can dissolve any more of the solute. If there is a saturation point, the point is distinct and characteristic of the type of materials and temperature of the solution.
- vii. The solution of an ionic material into water will result in an *electrolyte* solution. The ions of solute will separate in water to permit the solution to carry an electric current.

The best way to measure the amount of a solid material is usually to weigh it. The best way to find the amount of a liquid is to find the volume. The formula for solutions is:  $C V = n$ , where  $C$  is concentration in molar [ $\text{mol}/\text{dm}^3$ ],  $V$  is the volume in liters [ $\text{dm}^3$ ], and  $n$  is the number of mols of solute. Further,  $n = m/M_s$ , where  $m$  is the mass and  $M_s$  is the formula weight of the solute. Solving for the mass,  $m = C V M_s$ .

When preparing the raw material liquid for nHalo, first weigh the solid to get the mass. The concentration you want times the volume of solution times the formula weight of the solute will get you the mass of solute you need to weigh. Place the mass of solute in a volume measuring device such as a volumetric flask or a graduated cylinder. Use a small amount of water to dissolve the solute in the volumetric device. Add water to the volume desired and mix.

The act of dissolving a solid into a liquid is a process that happens on the surface of the particles of the solute. The smaller the particles (the larger the surface area) the faster the solute dissolves.

Expose the surface area of the solid to more solvent and the solute will dissolve faster. Mixing helps dissolve the solid.

Most solid materials will dissolve faster with increased temperature. Since the increased temperature increases the motion of the molecules, you can think of this effect as being similar to mixing.

*Solubility* is the amount of mass of a compound that will dissolve in a unit volume of solution. Aqueous solubility is the maximum concentration of a chemical that will dissolve in pure water at a reference temperature.

Solubility depends on the solute and salts with different amount of crystalline water generally have different solubility. Thus for example different copper salts have the following solutions to cold and hot water<sup>3</sup>:

| Solute  | Solubility to cold water<br>(g/100 cc) | Solubility to hot water<br>(g/100 cc) |
|---|--|---------------------------------------|
| Copper(I)chloride<br>CuCl   | 0,0062                                 |                                       |
| Copper(II)chloride<br>CuCl <sub>2</sub>   | 70,6                                   | 107,9                                 |
| Copper(II)chloride,<br>dehydrate<br>CuCl <sub>2</sub> ·2H <sub>2</sub> O                  | 110,4                                  | 192,4                                 |
| Copper(II)nitrate,<br>hexahydrate<br>Cu(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 243,7                                  | ∞                                     |
| Copper(II)nitrate, trihydrate<br>Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O     | 137,8                                  | 1270                                  |
| Copper(II)nitrite, basic<br>Cu(NO <sub>2</sub> ) <sub>2</sub> ·3Cu(OH) <sub>2</sub>       | insoluble                              | decomposes                            |
| Copper(I)sulfate<br>Cu <sub>2</sub> SO <sub>4</sub>                                       | decomposes                             |                                       |
| Copper(II)sulfate<br>CuSO <sub>4</sub>  | 14,3                                   | 75,4                                  |
| Copper(II)sulphate,<br>pentahydrate<br>CuSO <sub>4</sub> ·5H <sub>2</sub> O               | 31,6                                   | 203,3                                 |



It is thus very important to know the solute to be used (and to ensure that your vendor will provide you exactly the right material, especially be aware with hydrates). The solubility to alcohols is usually very different to solubility to water and depends on the alcohol used (most often methyl or ethyl alcohol).

The solvent used affects the temperature of the nHalo flame. Water as a solvent consumes energy and thus lowers the temperature of the oxy-hydrogen flame. Alcohols bring in additional energy and thus increase the flame temperature. In some cases, especially with high mass production rates, water may reduce the flame temperature too much for complete reactions to occur in the flame.

## 2.2. Atomization

For a complete reaction chain for the often low vapour pressure liquid precursor in the flame, the droplet size should be as small as possible when entering the hot flame. The small droplet size is ensured by a proper *atomization* of the liquid precursor.



Atomization is the process of breaking up a continuous liquid phase into discrete droplets. Atomizers may be classified into three broad groups: pressure atomizers, oscillating atomizers (typically ultrasonic) and twin-fluid atomizers<sup>4</sup>.

The commonest type of a pressure atomizer is the swirl-type atomizer. Entering a small cup through tangential orifices, the liquid swirls at high velocity. The outlet forms a dam around the open end of the cup, and the liquid spills over the dam in the form of a thin conical sheet, which subsequently breaks up into thin filaments and then droplets. In order to generate very small droplets (10  $\mu\text{m}$  or smaller), very high pressures (up to 1000 bar) need to be used, which makes this atomizer unpractical in most nHalo applications.

In ultrasonic atomizers electric waves are transformed into mechanical oscillations. Within the atomizer, these oscillations cause a regulated thin film of liquid to experience a minute wave action. These oscillations act to shear the liquid into finely atomized droplets. These atomizers cannot work on the burner outlet surface and thus their use in the nHalo process is currently in the r&d – phase. They may, however, be useful in some of the large-scale production applications of the future.

In a twin-fluid (two-fluid) atomizer, the liquid stream is exposed to a stream of gas flowing at high velocity. The atomizer may have an internal-mixing or an external-mixing configuration. In the internal-mixing, the liquid and gas mix inside the nozzle before discharging through the outlet orifice. In the external-mixing nozzle, the liquid stream is impacted by the high-velocity gas stream outside the nozzle. The internal type requires lower gas flows.

Most nHalo-applications use twin-fluid atomizers. The liquid orifice is positioned either concentric with, or at right angles to, the annulus from which the atomizing gas exits. Liquid is set into oscillation. Filaments of liquid are drawn out from the bulk of the solution. The filaments collapse to form droplets. The cloud of droplets may strike an obstruction in the system, which breaks the larger droplets into smaller ones. The final aerosol, really a very fine fog, is mixed with the oxygen/fuel gases and carried into the flame.

Atomization (nebulisation) is governed by such parameters as viscosity [ $\mu$ ], density [ $\rho$ ], and surface tension [ $\gamma$ ] of the liquid, the mass flow rate of the nebuliser gas [ $Q_{gas}$ ], and the liquid [ $Q_{liq}$ ], and the velocity of the atomizing gas [ $v$ ]. The volume-surface, or Sauter mean, diameter of the droplets [ $d_0$ ], in micrometers, is given by an empirical expression<sup>5</sup>:

$$d_0 = \frac{585}{v} \left[ \frac{\gamma}{\rho} \right]^{-0.5} + \left[ \frac{\mu}{(\gamma\rho)^{0.5}} \right]^{0.45} 1000 \left[ \frac{Q_{liq}}{Q_{gas}} \right]^{1.5} \quad (2.1)$$

Viscosity is a measure of the resistance of a fluid to deform under shear stress. It is commonly perceived as "thickness", or resistance to pouring. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. Thus, water is "thin", having a lower viscosity, while vegetable oil is "thick" having a higher viscosity. All real fluids (except superfluids) have some resistance to shear stress.

The SI physical unit of dynamic viscosity (greek symbol:  $\mu$ ) is the pascal-second (Pa·s), which is identical to  $1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ .

The cgs physical unit for dynamic viscosity is the *poise* (P) named after Jean Louis Marie Poiseuille. It is more commonly expressed, particularly in ASTM standards, as *centipoise* (cP). The centipoise is commonly used because water has a viscosity of 1.0020 cP (at 20 °C; the closeness to one is a convenient coincidence).

$$1 \text{ poise} = 100 \text{ centipoise} = 1 \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1} = 0.1 \text{ Pa}\cdot\text{s}.$$

$$1 \text{ centipoise} = 1 \text{ mPa}\cdot\text{s}.$$

Surface tension is the force acting on a liquid-gas interface resulting in thin film on the surface. It can be quantified as the force acting normal to the interface per unit length of the film at equilibrium which also equals the surface energy (the energy required to increase the surface area of the liquid by a unit amount). This force tends to minimize the area of the surface, thus explaining why drops and bubbles are round. In other words, surface tension  $\gamma$  is the energy that must be supplied to increase the surface area by one unit. The unit for surface tension is typically mJ/m (= mN/m<sup>2</sup> = dynes/cm)

As seen from the equation 2.1, the viscosity and surface tension of the liquid affect the mean droplet size. As these parameters are functions of the solute concentration, unanticipated changes in the droplet size can be avoided by preparing the precursor liquids similarly and avoiding very high salt concentrations.

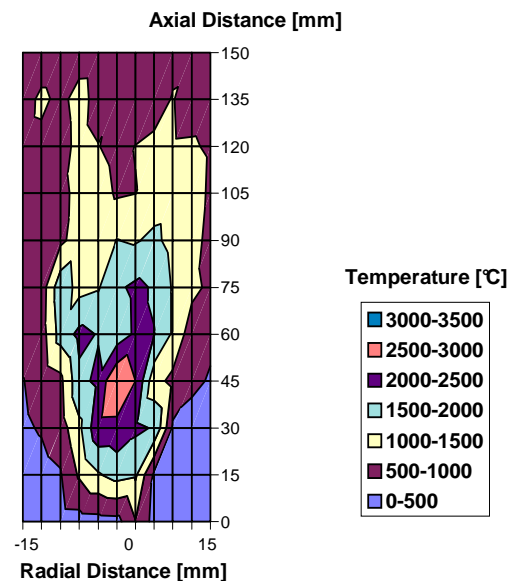
For pure solvents, without solutes, we have the following parameters:

| Solvent        | Viscosity [mPas] | Density [g/cm <sup>3</sup> ] | Surface tension [mJ/m] |
|----------------|------------------|------------------------------|------------------------|
| Water          | 1                | 1                            | 72                     |
| Methyl alcohol | 0,6              | 0,79                         | 23                     |
| Ethyl alcohol  | 1,2              | 0,77                         | 23                     |

Formula 2.1 predicts that the produced particle diameter decreases as a function of atomizing gas velocity and mass flow rate. However, in reality other parameters, especially stable combustion of the fuel gas must be taken into account. Typically, only hydrogen combusted next to the nozzle exit works without problems of the flame escaping the nozzle due to high fuel gas flow rate. therefore hydrogen is usually selected for atomization in the nHalo burner.

### 2.3. Reactions in the gas phase (in the flame)

When the precursor liquid is atomized into the flame various chemical reactions occur and nanosize particles are formed. The nHalo –flame is turbulent and has a wide temperature scale<sup>1</sup>, which can be divided into 1) hot zone, 2) intermediate zone and 3) cold zone<sup>6</sup>. Usually the burner and the process is tuned such that all the reactions occur in the hot zone. However, in special cases, e.g. in the production of layered particles, the mechanisms in the intermediate and cold zones can be used as an advantage and thus they are also revealed in the text below.



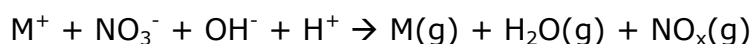
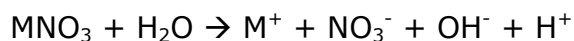
#### 2.3.1. Hot zone

The hot zone temperature is 1500 – 3000°C. Within this temperature range the metals used in the nHalo process usually vaporize easily. However, some metals,

like Palladium (Pd) and Lanthanum (La) show a very low vapour pressure at this temperature range and thus do not easily vaporize in the nHalo process.

The following examples are using water as the solvent. When alcohols are used for solvents, similar reactions mechanisms occur.

The metal is atomized in a water solution and in ionic form into the flame, where it evaporates (the droplet is assumed to be so small that all solvent evaporates immediately when the droplet enters the hot zone). Thus e.g. metal nitrates follow the reactions:



The vaporized metals condense to nanosize particles. In the presence of oxygen, the metal will condense as metal or as metal oxide (obviously oxidation requires the presence of oxygen, which is a normal situation in the nHalo process). The dominating mechanism can be approximated by comparing the changes in the Gibbs energy for metal condensation and for oxidation as a function of the temperature drop.

What is Gibbs energy? Useful energy, or energy available to do work, is of central interest because there is never a shortage of useful work to be done, and usually an insufficiency of useful energy to do it. Energy which is, or which can be, available to do useful work is called Gibbs free energy or more often simply free energy.

Free energy is a state function because it is formally defined only in terms of state functions, the state functions enthalpy and entropy, and the state variable temperature. The definition of free energy is:

$$G = H - TS$$

In the above equation  $H$  is the enthalpy,  $S$  is the entropy, and  $T$  is the absolute temperature.

A change in free energy  $\Delta G$  would then be given by  $\Delta G = \Delta H - \Delta(TS)$ .

When  $\Delta G$  is negative, energy is evolved (given up) in the process or reaction and the change can do useful work on something else. This is a spontaneous process, and is sometimes called an exergonic (energy-giving) process. When  $\Delta G$  is positive, energy is absorbed in the process or reaction and useful work must be done on the materials so that the reaction will occur. This is a nonspontaneous process, and is sometimes called an endergonic (energy-requiring) process.

Thus in comparing the different reactions paths in the nHalo flame (oxidation or metal condensation): *the reaction with larger drop in the Gibbs energy is more favourable.*

The changes in the Gibbs free energy can be calculated (approximated) by various chemical reaction and equilibrium software, like HSC Chemistry by Outokumpu Technology<sup>7</sup>.

For example silver condenses to metal silver particles when the temperature drops, but iron reacts with oxygen forming iron oxide particles.

If the metal does not evaporate easily, if the flame temperature is low or the thermal energy available is low, particles are formed directly from the metallic salt solution. The solvent and the nitrogen oxides (from the nitrate) will evaporate, but the metal forms a metal oxide directly in the droplet. The particles formed by this mechanism are usually much larger than nanosize.

Metallic salt (nitrate)  $\rightarrow M_xO_y(s)$

The best results in the nHalo process are usually achieved, when all the precursor material evaporates. This ensures the production of metal- or metal oxide particles with a very narrow particle size distribution and a nanometer range (10...100 nm) mean particle size.

The nucleation routes for metal and metal oxide particles are slightly different. In both cases the formation of particles or condensation on existing particles initiates when the gas is sufficiently supersaturated with respect to one or more components. This initial supersaturation is obtained in the nHalo process either by cooling (as in the case of silver) or by a chemical reaction that generates atoms or molecules with low vapour pressure (as in the case of e.g. iron oxide). For compounds with sufficient vapour pressure levels (like silver in the hot zone), nucleation is controlled by formation of stable molecular clusters. For a given supersaturation, a critical cluster size exists. Above this size, the cluster is stable and will continue to grow. Below the critical size, the cluster is unstable and will evaporate. The dynamics of the cluster size distribution is determined by the condensation/evaporation process. If the supersaturation is sufficiently high, the critical cluster size is small and homogeneous nucleation will occur. This mechanism is called evaporation-condensation controlled because of the influence of evaporation and condensation dynamics on the cluster distribution below the critical size.

If the supersaturation is extremely high, two molecules sticking together form a stable particle (B-molecule). Particle formation/growth is then controlled by collision of B-molecules. This is the case if the B-molecule has an extremely low vapour pressure. Metal oxides like  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ , etc. belong to the group of compounds with very low vapour pressure<sup>8</sup>.

### 2.3.2. Intermediate zone

The temperature in the nHalo flame is spatial and the flame is turbulent and thus all the precursor material does not necessarily enter the hot zone, especially if extremely high precursor feed rates are used. Metal in the droplets passing the intermediate zone does not necessarily vaporize. The metal ions in the droplet prefer to produce metal oxide rather than metal. These metal oxides tend to break at a relatively low temperature, so usually (when they enter the hot zone in the turbulent flame) they break and form metal vapour.

Metal salt solution  $\rightarrow \text{M}_x\text{O}_y(\text{s}) \rightarrow \text{M}(\text{g}) \rightarrow \text{M}(\text{s})/\text{M}_x\text{O}_y(\text{s})$

The metal oxides produced directly from the liquid phase may have a different crystal structure than the metal oxides produced through evaporation-condensation.

The reactions in the intermediate zone are complicated and they are difficult to study. However, in the normal nHalo operating mode the effect of the intermediate zone on the produced nanoparticles is marginal.

### 2.3.3. Cold zone

In the cold zone the droplet does not vaporize at all. In this case the solid particles will form as in spray-pyrolysis. The solvent from the droplet dries out, water and nitrogen oxides evaporate and metal or metal oxide particles – or metal salt crystals – are formed. The particles formed in the cold zone are typically dramatically larger than the particles formed in the hot zone. Thus these particles may severely affect the end product and should be avoided.

It is very unlikely that cold-zone particles are formed in the nHalo process. If this happens, it is usually a sign of deformation of the nhalo burner head, or sign of extremely high liquid feed rates (with a non-combustible liquid).

### 2.4. Particle interaction

For an aerosol, the coagulation of particles becomes important at high concentrations, above say  $10^6 \text{ cm}^{-3}$ .

In the nHalo-process typically up to 1 g/min of 50 nm particles is diluted to a gas volume of 100 SLM. This means a particle concentration of  $10^{11} \text{ cm}^{-3}$ , so the *coagulation* of particles in the nHalo process is inevitable.

Coagulation is highly influenced by the concentration. The time to reduce the concentration by a factor of 10 by Brownian coagulation is approximately 0,5 s when the initial concentration is  $10^{11} \text{ cm}^{-3}$ . This is the basic reason why high-concentration nanoparticle clouds cannot be effectively transferred inside tubes (without coagulation).



Particle collisions occur because of differences in particle velocities and several different mechanisms may lead to that. Brownian motion, velocity gradients in shear flow systems and external force fields are among the important mechanisms. Examples of external force fields are gravity or electrical fields. For particles in the submicron range, Brownian motion is the dominant coagulation mechanism with a collision frequency function several orders of magnitude larger than those of gravitational settling and shear.

Small particles suspended in a fluid undergo random translational motions due to molecular collisions. This phenomenon is referred to as the Brownian motion. The Brownian motion leads to diffusion of particles in accordance with Fick's law. i.e.,

$$J = -D \frac{dc}{dx} \quad (2.2)$$

where  $c$  is the concentration,  $J$  is the flux and  $D$  is the diffusion coefficient. The diffusion coefficient is inversely proportional to the particle diameter and thus nanoparticles show a much larger diffusion coefficient than micron-size particles as seen from the table below<sup>9</sup>.

Table 2-I Particle mass diffusivity

| $d$ (nm) | $D$ (cm <sup>2</sup> /s) |
|----------|--------------------------|
| 10       | 5,24 x 10 <sup>-4</sup>  |
| 100      | 6,82 x 10 <sup>-6</sup>  |
| 1000     | 2,74 x 10 <sup>-7</sup>  |
| 10000    | 2,38 x 10 <sup>-8</sup>  |

The number of collisions,  $R_{ij}$ , per unit time per unit volume between two different particle classes of size  $d_{p1}$  and  $d_{p2}$  with corresponding volume-based concentrations  $N_1$  and  $N_2$  is given by

$$R_{12} = \beta(d_{p1}, d_{p2}) N_1 N_2 \quad (2.3)$$

In this equation,  $\beta$  is the collision frequency function, having the dimension  $[\text{m}^3\text{s}^{-1}]$ .

An approximation of  $\beta$ , valid over the entire particle size range is:

$$\beta = 2\pi(D_{p1} + D_{p2})(d_{p1} + d_{p2}) \left\{ \frac{d_{p1} + d_{p2}}{d_{p1} + d_{p2} + 2g_{12}} + \frac{8(D_{p1} + D_{p2})}{\bar{c}_{12}(d_{p1} + d_{p2})} \right\}^{-1} \quad (2.4)$$

$$g_{12} = \sqrt{g_1^2 + g_2^2}, \quad g_i = \frac{(d_{pi} + l_i)^3 - (d_{pi}^2 + l_i^2)^{3/2}}{3d_{pi}l_i} - d_{pi}, \quad l_i = \frac{8D_{pi}}{\pi \bar{c}_i} \quad (2.5)$$

$$\bar{c}_{12} = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}, \quad \bar{c}_i = \sqrt{\frac{8k_bT}{\pi n_{pi}}}, \quad m_{pi} = \rho_{pi} \frac{\pi}{6} d_{pi}^3, \quad i = 1,2 \quad (2.6)$$

In the equations above,  $d_{p1}$  and  $d_{p2}$  are the diameters of the colliding particles and  $\bar{c}_i$  is the mean particle speed. The particle diffusion coefficient,  $D_{pi}$ , can be calculated by:

$$D_{pi} = \frac{k_bT}{3\pi\mu d_{pi}} \left[ \frac{5 + 4Kn_i + 6Kn_i^2 + 18Kn_i^3}{5 - Kn_i + (8 + \pi)Kn_i^2} \right] \quad (2.7)$$

The Knudsen number,  $Kn_i$ , is the ratio of the mean free path of the gas,  $\lambda_g$ , and the particle radius:

$$Kn_i = \frac{2\lambda_g}{d_{pi}}, \quad \lambda_g = \frac{\mu_g}{\rho_g} \sqrt{\frac{\pi M_g}{2RT_g}} \quad (2.8)$$

where  $\mu_g$ ,  $\rho_g$  and  $M_g$  are the gas viscosity, gas density and molar mass of the gas respectively. The mean free path of the gas is the average distance travelled by a molecule between two successive collisions. At STP the mean free path of the gas molecules is on the order of 100 nm. This means that the Knudsen number for nanoparticles (10...100 nm) is 2-10. This means that the particle motion falls to

the free-molecular range and interaction between the particle and the gas can be calculated from molecular collision probabilities.

During the first stages of the nucleation/coagulation process, the particles are very small. When two particles/aggregates collide and stick together, they can either retain their individual shape or fuse/diffuse together thereby forming a spherical particle. The latter sintering process is usually called *coalescence*. The driving force for coalescence is the surface tension, which strives to reduce the aggregate surface area. The coalescence occurs in the hot zone of the nHalo process and is the driving force (with coagulation) to produce spherical particles with 10 – 100 nm diameter.

An *aggregate* is a cluster of many smaller primary particles. Most of the aggregate formation by coagulation takes place outside the hot zone. Coagulation at lower temperatures results in complicated dendritic structures.

## 2.5. Particle deposition

### 2.5.1. Impaction

When the born particle moves towards the substrate, the force per area needed to move the particle towards the substrate can be approximated from:

$$\frac{F}{area} = \frac{3\pi\mu\nu a^2}{2h^3} \quad (2.9)$$

where  $\mu$  is the viscosity of the gas,  $\nu$  is the particle velocity  $a$  is the radius of the (spherical) particle and  $h$  is the distance between the particle and the substrate.

The formula shows that the resistance force becomes infinitely large as  $h \rightarrow 0$ . that implies that the particle would never contact the substrate. However, the particle will indeed hit the substrate due to the presence of van der Waals force. The van der Waals force per unit area between two surfaces can be approximated from<sup>10</sup>:

$$\frac{F}{area} = -\frac{A}{6\pi h^3} \quad (2.10)$$

and equating these two equations we find the criteria for the velocity

$$v = \frac{A}{9\mu\pi^2 a^2} \quad (2.11)$$

where  $A$  is called Hamaker's coefficient and equals:

$$A = \pi^2 q_1 q_2 \lambda_{1,2} \quad (2.12)$$

$\lambda_{1,2}$  is the London's constant, whose value depends on the atomic numbers of the two interacting atoms and  $q_1$  and  $q_2$  are the amounts of 'interacting' atoms in the particles.

Equation 2.10 shows that the required velocity for deposition increases sharply when the particle radius decreases. Thus the deposition of 30 nm particles requires 10-times higher velocity than deposition of 100 nm particles.

The Hamaker's coefficient for a 10...100 nm particle is about  $1 \text{ eV} \approx 1,6 \times 10^{-19} \text{ J}$ <sup>11</sup>. Thus the velocity to deposit 30 nm particles on a substrate is roughly one meter per second. Velocities much larger than this may lead to the rebound of particles from the surface.

### 2.5.2. Brownian motion

It is important to note that although the gas velocities at the nHalo burner exit are about two decades higher than the velocity required for inertial deposition, this is not the case anymore close to the substrate surface. The velocity should be of this order at the *stop distance* from the substrate surface in order for the particles to be trapped. Stop distance is defined as the distance that a particle having an initial velocity of  $v_0$  will travel in a quiescent fluid due to its inertia. Thus, a particle diffusing to one stop distance from the wall is assumed to have sufficient inertia to penetrate the viscous sublayer and reach the substrate. The stop distance can be calculated as<sup>12</sup>:

$$S = v_0 \tau_p \quad (2.13)$$

where  $\tau_p$  is the particle relaxation time given by:

$$\tau_p = \frac{\rho_p d_p^2}{18\mu} \quad (2.14)$$

For the velocity of 1 meter/second the stop distance is roughly the diameter of the particle. As the particles with a Knudsen number larger than one will follow the gas flow lines, it will be very difficult to create a velocity perpendicular to the surface of 1 m/s at 100 nm distance from the surface. Thus a turbulent gas flow is typically required to enhance deposition on the surface. Turbulent gas flow ensures that the particle flow will pass close to the substrate surface and thus Brownian motion will bring the particles so close to the surface that they get attracted by van der Waals force.

### 2.5.3. Thermophoresis

In addition to the Brownian motion, a very important deposition mechanism in the nHalo –process is *thermophoresis*. Small particles present in a temperature gradient are driven away from regions of higher temperature. For particles with  $Kn \gg 1$ , the media atoms impact the particle at a higher rate on the hot side driving the particles towards the cold end of the temperature gradient. For  $Kn \gg 1$ , the thermophoretic velocity,  $v_{th}$ , is independent of particle size and is given by:

$$c_T = \frac{-3\nu\Delta T}{4T\left(1 + \frac{\pi\alpha}{8}\right)} \quad (2.15)$$

where  $\alpha$  is the accommodation coefficient that gives the fraction of gas molecules that leave a particle surface after equilibrating with the surface, i.e. after imparting their excess thermal energy to the particle. The accommodation coefficient is typically 0,9 for nanoparticles.

Kinematic viscosity,  $\nu$ , has SI units ( $m^2 \cdot s^{-1}$ ). The cgs physical unit for kinematic viscosity is the *stokes* (abbreviated S or St). It is sometimes expressed in terms

of *centistokes* (cS or cSt), 1 stokes = 100 centistokes =  $1 \text{ cm}^2 \cdot \text{s}^{-1} = 0.0001 \text{ m}^2 \cdot \text{s}^{-1}$ .

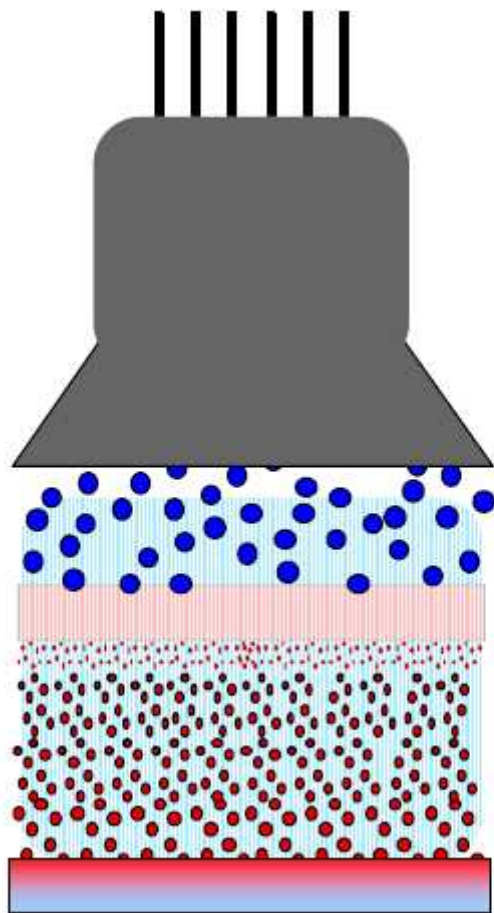
Conversion between kinematic and dynamic viscosity, then, is given by  $\nu\rho = \mu$ .

#### 2.5.4. Electrical forces

Charging of nanoparticles can occur due to ion attachment, static charge buildup and thermionic charging, which means heating the particles to a point of electron or ion release. This phenomena is likely to occur in the nHalo process due to the high flame temperature. The actual charge on the particles as well as unipolar or bipolar charging is a function of the raw materials and gases used, flame temperature, gas velocities, etc. and the particle charging in the nHalo process has not been completely studied. However, naturally occurring charges in the nHalo particles as well as additional particle charging combined with externally arranged electrical fields or substrate charging can be used as an advantage in the nHalo deposition process.

### 3. Epilogue

Hot Aerosol Layering Operation (nHalo) is based on the combustion of gaseous and atomised liquid raw materials in an atmospheric oxy-fuel flame. This evaporation-condensation controlled method produces metal oxides, noble metal nanoparticles and combinations thereof. The flexibility in the raw material feed allows for great freedom of incorporating materials with very different vapour pressures. A turbulent flame provides efficient mixing of the raw materials leading to homogeneous nanoparticles. Rapid quenching and short residence time produces small particles with a narrow particle size distribution, i.e. monodisperse particles. The figure below shows the different regions of the nHalo process.



①

*Droplet-to-particle-to-coating conversion in the nHalo process.*

*1) Raw material feeding*

*2) Droplet generation*

*3) Droplet and metal evaporation*

②

*4) Reaction and flash condensation*

③

*5) Particle growth*

④

*6) Deposition on the surface*

⑤

*7) Diffusion and dissolution.*

⑥

⑦

The formation of nanoparticles from micron-sized droplets is a complicated process. Various parameters affect the formation process, e.g., the vapour pressure of the metals, flame temperature, gas velocities, the droplet route through the flame and the Gibbs free energy of the raw materials. On one hand, the smaller the produced droplet is, the more complete is the evaporation of the liquid. On the other hand, small droplets tend to coagulate together forming larger particles. In the nHalo process the liquid feed rate and the droplet size are optimised and the typical droplet concentration is in the order of  $10^8 \text{ cm}^{-3}$ .

The basic idea of the nHalo process can be considered to be one where all the reactants required in the preparation of nanoparticles are first brought to a vaporous form, i.e. gas phase. Condensation of reduced components from the gas phase to a solid phase occurs extremely rapidly in such a manner, that all components contained in the reactants and required in forming the nanoparticles are brought simultaneously to a supersaturated state, in which case the

composition of solid particles is very homogeneous. The afore-mentioned homogeneous composition of particles refers to, firstly, that different particles have the same composition, and secondly, that the local inner composition of the individual particles is homogeneous, i.e. all components are equally divided over the entire volume of each individual particle. The above mentioned rapid condensation of the components of the reactants is achieved either by fast oxidation of reactants and/or by fast adiabatic expansion of the gas flow of the reactants.

The size of the nanoparticles in the nHalo process depends mainly on the mass feed rate. The shape of the particle size distribution remains constant, but the mean diameter increases with increasing mass feed rate. The material produced has little effect on the mean particle diameter and particle size distribution.



## 4. References

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