

FORMATION OF NANOPARTICLES BY CVD TECHNIQUE

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ABSTRACT

A concept of formation of nanosized particles by CVD is presented in the light of laminar transport phenomena. The essential steps: (I) nucleus formation, (II) nucleus growth and (III) collection of nanosized powder, are explained from the theoretical point of view. Also, three basic types of particles: (i) semi-homogeneous /nucleus core with same surface layer/; (ii) "simple" heterogeneous /nucleus core with different surface layer produced by "simple" CVD/ and (iii) heterogeneous /nucleus core with different surface layer produced by surface chemical reactions during the CVD/, are discussed.

The experiment of the "simple" heterogeneous nanosized Ni-Al₂O₃ particle formation [6,7] is described as example of presented theoretical approach. The starting powders of AlCl₃·2H₂O and NiCl₂·6H₂O (with 0,1 mass % Pd in form of PdCl₂) are separately reduced by the hydrogen-nitrogen atmosphere in the horizontal, tubular hot-wall reactor, that is organized within the three different temperature zones. X-ray and SEM analysis are used for characterization of the obtained powders.

Keywords: nanosized particles, laminar transport phenomena, formation modeling

1. INTRODUCTIN

Ultrafine grained ceramics, metals and alloys have superior materials properties which have attracted increasing interest. It is well known, that powder refinement is one approach to reducing the frequency of microstructural inhomogeneties in the parts.

Formation of nanosized particles by CVD under laminar regime (*Laminar CVD*) is imagined as a process in horizontal, tubular hot-wall reactor. Minimum three different (temperature and/or flow) zones are required: *zone I* - nucleus formation, *zone II* - nucleus growth and *zone III* - collection of nanosized powder, **Figure 1**. Herein there are: (1) a typical tube flow and (2) nanosized spheres moving relative to a fluid with velocity in laminar regime. Thus, we have two various flow systems that are quite different, **Table 1** [1].

In laminar or streamline flow the fluid's motion seems to be the sliding of laminations of infinitesimal thickness relative to adjacent layers, and that the

hypothetical particles in the layers move in predictable paths or streamlines [2]. In our case the “hypothetical particles” are the real nanosized particles in growing progress. The size of the particles does not disturb the streamlines. So, we are in laminar nano-area. It is well known that Stokes’ law can be applied up to $Re = 1$ for spheres. In our case $Re \ll 1$, so we have no information about the real transport and chemical rate phenomena, because of problems with experimental measurements. It seems that the particle may be hanged or hovered in the fluid ($f \rightarrow \infty$).

The forced convection heat transfer from and to the particle/sphere around which a fluid is flowing, can be well defined as [1,2]:

$$Nu = 2.0 + 0.60Re_f^{1/2}Pr_f^{1/3} \quad (1)$$

Table 1 - Comparison of flow systems via friction factor (or drag coefficient) f , adapted from [1]

Tube flow	Spheres moving relative to a fluid
Well-defined laminar-turbulent transition at $Re = 2100$	The f -curve exhibits no well-defined laminar-turbulent transition
(for smooth tubes) the only contribution to f is friction drag	Contributions to f owing to both friction drag and form drag
There is no boundary layer separation	There is a kink in f -curve associated with a shift in the separation zone
For $Re < 2100 \Rightarrow f=16/Re$, $Re = D_{tube}(v)\rho/\mu$ Hagen-Poiseuille law	For $Re < 0.1 \Rightarrow f=24/Re$, $Re = D_{sphere}(v_{\infty})\rho/\mu$, Stokes’s law, creeping flow

At low Reynolds number or motionless fluid this equation predicts $Nu = 2$ that has been confirmed by numerous experiments.

Similarly, mass transfer coefficient during forced convection can be analogly presented as [1,2]

$$Sh = 2.0 + 0.60Re_f^{1/2}Sc_f^{1/3} \quad (2)$$

Also, at low Reynolds number or motionless fluid this equation predicts $Sh = 2$ (see Appendix).

Heat and mass transfer are accompanied with chemical reactions around as well as at the surface of the growing particle.

2. MODELS OF PARTICLES FORMATION [3]

We can imagine three essential steps of the process: nucleus formation (*zone I*), nucleus growth (*zone II*) and collection of nanosized powder (*zone III*) presented on **Figure 1**.

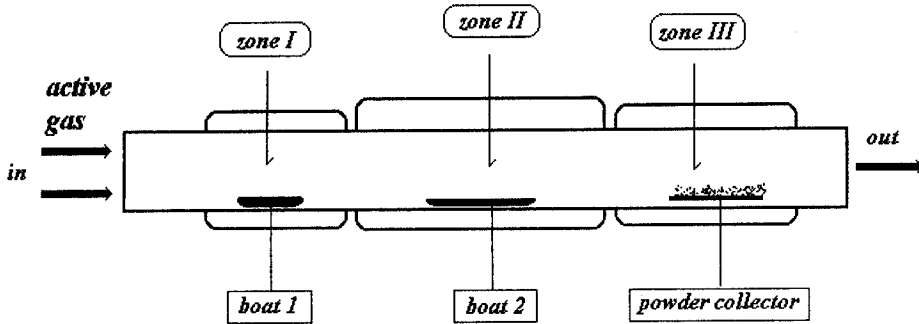


Figure 1 - Schematic presentation of the horizontal reactor system for laminar CVD

2.1. Nucleus formation (zone I)

The nucleation process as a sequence of additions of single molecules to the developing embryo can be defined by the critical nucleus radius [4,5]:

$$r^* = -2\sigma/\Delta G_v \tag{3}$$

where σ is the surface tension and ΔG_v is the free energy change per unit volume produced in the condensation process or

$$\Delta G_v = -(kT/\Omega) \ln(p/p_0) \tag{4}$$

where Ω is the molecular volume in the solid and p_0 is the equilibrium vapor pressure of the solid at the temperature T.

In the light of an active atmosphere flow past a nucleus we can obtain the friction factor (drag coefficient) for laminar flow past a sphere/nucleus [1,2]

$$f = 24/Re_{D(n)} \tag{5}$$

where $Re_{D(n)} = D(n)V_\infty/\nu$ is the Reynolds number, $D(n)$ diameter of nucleus, V_∞ bulk velocity of an active atmosphere and ν kinematic viscosity. Because of nanosized nucleus ($Re_{D(n)} \approx 0$) the friction factor (drag coefficient) is so great that the nucleus is in rest relative to the bulk velocity.

2.2. Nucleus growth (zone II)

Generally, we have three possibilities of nucleus growth:

- (i) semi-homogeneous (nucleus core with same surface layer);
- (ii) "simple" heterogeneous (nucleus core with different surface layers produced by "simple" CVD) and
- (iii) heterogeneous (nucleus core with different surface layers produced by surface chemical reactions during the CVD)

Semi-homogeneous and "simple" heterogeneous growth will be explained via *thermal balance* concept. On the other hand, the heterogeneous growth will be described via *mass balance* concept.

2.2.1. Thermal balance concept

When a nucleus enters the zone II, a thermal boundary characterized by a very steep temperature gradient (ΔT) will form around it. This gradient may exhibit strong deviation from chemical and kinetic equilibrium. The heat transfer coefficient (h) from the nucleus may be calculated from the well known correlation (when $Re_{D(n)} \approx 0$) [1,2]:

$$Nu = hD/k = 2 \quad \text{or} \quad h = k/r \quad (6)$$

where Nu is Nusselt number, k thermal conductivity and $r = D_s/2$ ($r^* < r < r_{end}$).

Thus, the difference of heat leaving from the particle is:

$$dQ = -4\pi r^2 (k/r) (\Delta T) dt \quad (7)$$

Appropriate mass deposited from the vapor:

$$dG = dQ/L = -4\pi r^2 dr \rho_s \quad (8)$$

where L is the latent heat of condensation/sublimation and ρ_s is the density of the deposited substance.

The balance (8) gives the time for the particle growth from r^* to r_{end} :

$$t = [(L\rho_s)/(2k\Delta T)](r_{end}^2 + r^{*2}) \quad (9)$$

Also, the finale solution has the form:

$$r_{end} = [(2k\Delta T)t/(L\rho_s) + r^{*2}]^{1/2} \quad (10)$$

that gives the possibility of particle size evolution in respect of time.

2.2.2. Mass balance concept

Mass balance of solid layer deposited on the nucleus, produced by surface chemical reactions during the CVD:

$$d \left(\rho_s \frac{4}{3} r^3 \pi \right) = K_s 4\pi r^2 dt \quad (11)$$

or

$$\frac{dr}{dt} = \frac{K_s}{\rho_s} \quad (12)$$

where: K_s is overall rate of formation of solid layer ($\text{kg/m}^2\text{s}$) and ρ_s is density of the deposited substance.

We can define K_s as:

$$K_s = \xi \frac{\beta k}{\beta + k} C_o \quad (13)$$

or

or

$$Ks = \xi \frac{1}{\frac{1}{D} \left(\frac{2r}{Sh} + \frac{D}{k} \right)} Co \quad (14)$$

where:

ξ - stoichiometric coefficient of homogeneous reaction of solid surface formation from volume,

Co - local bulk concentration of characteristic gas constituent at temperature To ,

$k = \eta k(o)$ - "real" heterogeneous chemical reaction rate coefficient at To ,

$k(o)$ - "pure" heterogeneous chemical reaction rate coefficient at To ,

η - internal effectiveness,

$\beta = a\beta(o)$ - "real" interphase mass transport coefficient ($\beta = ShD/D_s$),

$\beta(o)$ - "pure" interphase mass transport coefficient,

a - external (superficial) surface to volume ratio.

So, the time for the particle growth from r^* to $r(end)$ is:

$$t = \rho_s \int_{r^*}^{r(end)} \frac{dr}{Ks} \quad (15)$$

or

$$t = \frac{\rho_s}{\xi DCo} \left[\int_{r^*}^{r(end)} \frac{2r}{Sh} dr + \int_{r^*}^{r(end)} \frac{D}{k} dr \right] \quad (16)$$

If $r^* \rightarrow 0$ and $Sh = 2$ we have the simplified solution:

$$t = \frac{\rho_s (r(end))^2}{2\xi DCo} \left[1 + \frac{2D}{k r(end)} \right] \quad (17)$$

as a possibility for calculation of time for particle formation from r^* to $r(end)$.

2.2.3. Collection of nanosized powder (zone III)

Finally, the formed nanosized particles are collected at temperature lower than in zone II; on specially designed folders. It must be mentioned, that a great problem with the laboratory reactor is the cleaning of the reactor tube, which is necessary after each experiment in order to avoid the accumulation of reaction products.

3. EXAMPLE (an experiment on "simple" heterogeneous particle formation [6,7])

Supported catalysts are the most widely used in industry and consist mainly of a support (here alumina) over which an active substance, usually a metal (here Ni) is dispersed. The catalysts characteristics as: activity, selectivity,

stability, mechanical strength and thermal conductivity, are closely dependent on composition and processing technology.

Ni/alumina catalysts are usually produced by impregnation of alumina support with nickel nitrate, calcined in air to decompose the nitrate into oxide, which is then reduced to metallic Ni under hydrogen (activation). They also can be produced by careful coprecipitation of nickel carbonate and aluminum hydroxide from a solution of the corresponding nitrates by adding sodium carbonate, followed by remaining steps (drying, calcining and activation). Recently, the combustion synthesis of multicomponent ceramic oxides has gained reputation as a preparation process to produce homogeneous, very fine, crystalline and unagglomerated powders, without the intermediate decomposition and/or calcining steps [8].

In this example, the production of the nanosized Ni-Al₂O₃ powders for Ni/alumina catalysts by CVD technique is shown as "simple" heterogeneous particle formation.

The starting powders of AlCl₃·2H₂O and NiCl₂·6H₂O (with 0,1 mass % Pd in form of PdCl₂) were separately reduced by the hydrogen-nitrogen atmosphere in the horizontal, tubular hot-wall reactor, that was organized within the three different temperature zones, (see **Figure 1**). X-ray and SEM analysis were used for characterization of the obtained powders.

A horizontal, tubular hot-wall reactor was used for the experiment. Quartz tube with diameter of 29 mm and 2 m length was placed into reactor with three independent zones. AlCl₃·2H₂O (boat I/zone I) and NiCl₂·6H₂O (boat II/zone II) were used for preparation of Ni-Al₂O₃ powders by reduction in H₂-N₂ atmosphere (hydrogen flow rate 60 l/h and nitrogen flow rate 20 l/h). Appropriate amount of Pd (0,1 mass percent of Pd in form of PdCl₂) was added in boat II. AlCl₃ was vaporized at temperature from 180°C in the first zone; NiCl₂ at temperature from 950°C in the second zone, while the particles of Ni-Al₂O₃ powders were deposited/collected in zone III. A stream of nitrogen gas was introduced at the front end of reactor tube to improve mixing and prevent back flow of reactant gases. HCl was absorbed in water on the other end of the tube.

Descriptive nanosized image of Ni-Al₂O₃ particles formation is shown on **Figure 2**. Results of thermal balance concept indicate that the residence time of the reaction species in **zone I** is about 94 sec and in **zone II** about 80 sec.

In previous investigations the addition of Pd has been used to increase H₂ absorption of Ni, since Ni itself belongs to group of poor H₂ absorbers. Due to presence of Pd, H₂ spillover effect can occur, where hydrogen in a molecular form is transformed into reactive atoms, thereby intensifying the reduction process [9].

A scanning electron microscope JEOL-5300 was used for the study of particle size and shape. An X-ray study of prepared powder has been done, using $\text{CuK}\alpha$ radiation and graphite monochromator, on the diffractometer PW 1710. The qualitative characterization of powders was performed using energy dispersive spectroscopy (EDS) analysis with a Si (Bi) X-Ray detector. An EDS system QX 2000/S (Oxford Instruments, UK) connected with SEM and computed multi-channel analyzer MCA were used for the analysis.

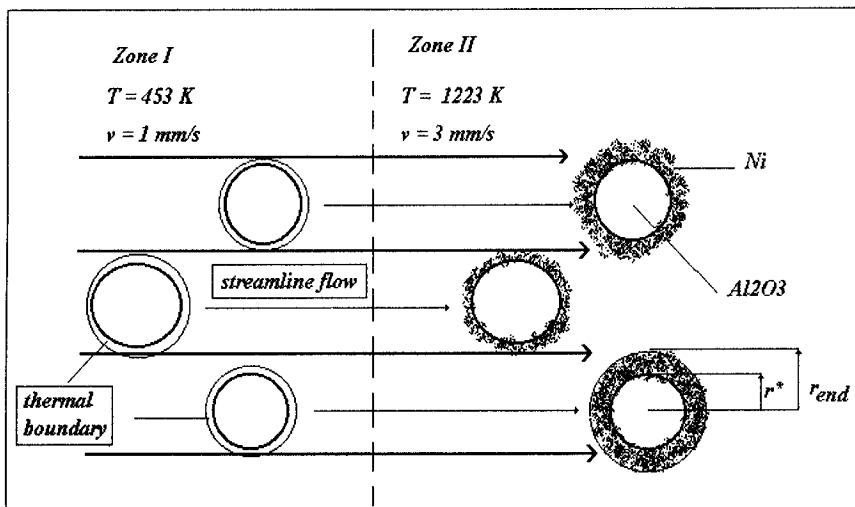
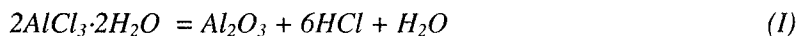


Figure 2 - Descriptive model of Ni- Al_2O_3 nanosized particles formation

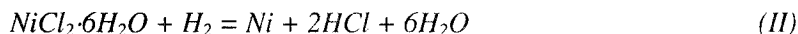
3.1. Mechanism of chemical formation

Mechanism of forming Ni- Al_2O_3 particles from gaseous phases is very complex. Precursors compounds have different temperatures of evaporating: (AlCl_3 : 180°C and NiCl_2 : 970°C), as well as different evaporation rates which have to be tuned in with aim to obtain fine particles from gaseous phase. Process of dehydration is also preset during this process, and it is necessary to provide conditions which will enable all wishful reactions of transformation to occur in short time, during gaseous mix stay in reaction zone.

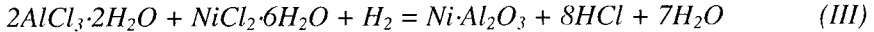
Decomposition of $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ is a process, which takes place between 300°C and 950°C at the technologically sufficient rate according to following equation:



The reduction of nickel chloride which involves the vapor-phase reduction forming ultrafine particles of nickel can be presented as follows:



Process of powder forming of Ni-Al₂O₃ can be represented with overall reaction:



With addition of Pd processes of decomposition of Al₂O₃·2H₂O and reduction of NiCl₂·6H₂O are intensified.

3.2. Results

X-ray analysis of Ni-Al₂O₃ powders produced by CVD method, in hydrogen-nitrogen atmosphere and the temperature interval from 180 to 950°C, is illustrated in [7]. EDS analysis confirmed this results. Peaks on X-Ray diagram points that metallic nickel and aluminium oxide are widely present in the sample of Ni/Al₂O₃ powder. SEM analysis of Ni/Al₂O₃ powder (**Figure 3.**) shows relatively rounded spherical particles (0,1 μm in size) as well as unagglomerated powder sample. These results confirm a positive effect of Pd. This effect is a consequence of the dissociation and spillover of hydrogen and is not only in decrease in particle size, but in the production of particles of uniform shape.

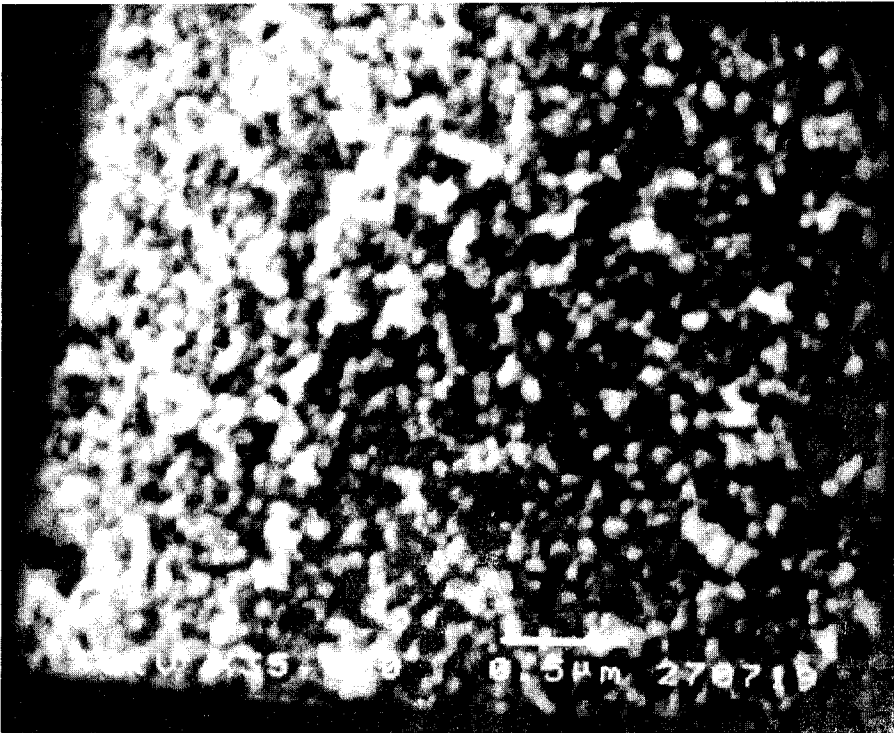


Figure 3 - SEM analysis of Ni/Al₂O₃ powder

4. CONCLUSION

The formation of nanosized powders by laminar CVD is satisfactorily modeled with the three-zone strategy, assuming intermediate species. The size of the particles is governed by the residence time of the reaction species in the zones, which in practice depends on the reactants' flow rates, the diameter of the inlet and cell pressure. Varying the flow rates of the reactants merely changes the velocity of the reacting species, and thus their residence time in the zones.

So, the size of particles is adjusted according to their "life" time in the reaction zones. For zone I the nucleation theory is appropriate, due to the small dimensions of the critical nuclei. For zone II the "thermal" and "mass balance" models provide a satisfactory agreement with experimental results.

Finally, the "simple" heterogeneous fine Ni-A₂O₃ particle formation, prepared from AlCl₃·2H₂O and NiCl₂·6H₂O powders under H₂-N₂ atmosphere by laminar CVD, is described as example of presented theoretical approach. Addition of Pd was necessary because of Ni reduction (spillover effect). Obtained grain size is 0,1 μm and the samples are anagglomerated. X-ray analysis detected metallic nickel and aluminum oxide that are widely present in the Ni/Al₂O₃ sample.

APPENDIX

Summary of Dimensionless Numbers

HEAT TRANSFER	MASS TRANSFER
$HD_s/k = 2.0 + 0.60(D_s V_\infty \rho_f / \eta_f)^{1/2} (C_p \eta_f / k)^{1/3}$	$Sh = 2.0 + 0.60 Re_f^{1/2} Sc_f^{1/3}$
$Re = D_s V_\infty \rho_f / \eta_f$ Reynolds number	$Re = D_s V_\infty \rho_f / \eta_f$ Reynolds number
$Nu = h D_s / k$ Nusselt number	$Sh = k_M D_s / D$ Sherwood number
$Pr = \nu / \alpha$ Prandtl number	$Sc = \nu / D$ Schmidt number
$h = k / r_s$ for $Re \approx 0$	$K_M = D / r_s$ for $Re \approx 0$

Parameters for dimensionless numbers:

C_p : specific heat, J kg⁻¹ K⁻¹

D : diffusion coefficient, m² s⁻¹

$D_s = 2r_s$: diameter of the solid particle surrounded by the fluid with diffusion coefficient D , m

h : heat transfer coefficient, W m⁻² K⁻¹

k : thermal conductivity, W m⁻¹ K⁻¹

$k_M \equiv \beta$: mass transfer coefficient, m s⁻¹

Greek symbols:

$\alpha = k / \rho C_p$: thermal diffusivity, m² s⁻¹

η_f : fluid viscosity, N s m⁻²

ρ_f : fluid density, kg m⁻³

$\nu = \eta_f / \rho$: kinematic viscosity, m² s⁻¹

Subscripts:

s : solid

f : in bulk of fluid

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