SYNTHESIS AND MEASUREMENT OF ULTRAFINE PARTICLES

Proceedings of the International Workshop on the Synthesis and Measurement of Ultrafine Particles, held in Delft on May 28-29, 1993

Editors

J.C.M. Marijnissen S. Pratsinis

foreword by S.K. Friedlander

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FOREWORD

I was very pleased when the organizers of this Workshop invited me to write a foreword. The reason is simple to explain. The synthesis and measurement of ultrafine particles is at the frontier of aerosol science and technology. From a scientific point-of-view it combines the field of aerosol dynamics, which we aerosol scientists have pioneered over the last twenty five years, with aspects of solid state physics and chemistry at the nanometer scale. We would like to have reliable methods for predicting, hence controlling, the properties of solid nanometer particles including particle size and solid state properties. This is done now almost entirely by trial and error. Combining aerosol dynamics with solid state chemistry and physics will be a very challenging scientific task, both theoretically and experimentally.

However, the case for working in this field goes beyond the science to the applications. Solid particles in the nanometer size range have very special properties compared with bulk materials or even coarse particles. These special properties encompass mechanical, chemical, thermodynamic and optical behaviour. There is an interest in generating such particles on a pilot scale for commercial testing. If commercial applications can be demonstrated, the next step will be the scale-up of production. This will most likely be accomplished using aerosol flow reactors whose design will depend on a combination of aerosol dynamics and solid state processes, as explained above, together with fluid mechanical factors.

Finally, these new developments will have direct applications in pollution control, minimizing particulate emissions from high temperature processes including coal combustion, incineration, metallurgical processing and nuclear reactor accidents. The challenge is to engineer size distributions to reduce mass concentrations in the size range of the efficiency minimum for gas cleaning devices.

Hence I congratulate the organizers of this Workshop on their vision in choosing a topic of such great scientific interest and, potentially, such important technological applications.

Sheldon K. Friedlander Department of Chemical Engineering, UCLA I was wray pleased when the objectivers of the "correction multice to to write a forewood, "For their tracer is simple to explain. The contournant and measurement of obtaining particlas is of the forming of accessed attention and technology. "The excitation have pleased over the last offer field of accessed attention and technology. "The excitation have pleased over the last accessly for years, will associate the action of physics and technology accessing properties of could have to have related and physics and the predicting basics according the properties of could have to have related to the predicting basics according, the properties of could have a contractive broughing periods into predicting basics according, the properties of could have another to the broughing periods into accessing the properties of could have a contractive broughing periods into a size proportion. This is done now atoms antitety by total and an on. Counting provide and properties with date distances, and physics with and an on. Counting provide and, both intermedially and externation of the write and an on. Counting provide and, both with date distances and the second of the providence of the size properties and the second of the second of the providence of the size properties.

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INTRODUCTION

The Workshop on Synthesis and Measurement of Ultrafine Particles in Gas Flows

This workshop brought together scientists and engineers working with ultrafine particles in gases. These particles are important in industrial processes and in air pollution. Lightguides are made by fusion of agglomerates of ultrafine silica particles and subsequent drawing of the fiber. More than 2 millions tons of ultrafine titania particles are made each year for paints. Ultrafine particles constitute the starting point for the formation of particulate pollutants that degrade the air quality. Ultrafine particles serve as the catalyst for production of free radicals that contribute to the destruction of the ozone layer in the poles. Fluid particle interactions play a key role in gas phase synthesis of films and powders. Depending on the end use of these materials, laminar or turbulent flows are used. Today aerosol processes are used for large scale production of materials (pigmentary titania, fumed silica and optical fibers). Aside from these well-established applications there is strong research interest in developing new vapor phase processes for the manufacture of structural & electronic ceramics, nanophase materials, fullerenes, diamonds, metals, catalysts and superconductors.

The workshop opened by a lecture on the controlled production of ultrafine particles. During ultrafine particle synthesis the maximum process temperature is more important than the cooling rate of the aerosol because sintering is completed before a significant reduction of the process temperature (Friedlander, UCLA, USA). Large production rates of ultrafine particles formed either by condensation (di-ethyl-hexyl-sebacate) or by chemical reaction (titanium hydroxide) can be achieved in free turbulent jets (Koch, Fraunhofer Institute, Hannover, Germany). The mass flux of the aerosol precursor and the carrier gas flow rate largely determine the product powder size distribution as particle formation and growth are dominated by coagulation. Production of nanoparticles with controlled characteristics at large production rates is crucial for fully exploring their applications. A new design of the inert gas condensation method was presented that not only resulted in higher production rates than the conventional design but also reduced the spread of the distribution of the product particles (Gleiter and Haas, Univ. Saarlandes, Germany). Improved design of the gas flow through a set of two liquid nitrogen cooled plates was credited with the advantages of the new design. For the first time, synthesis of SnO₂ particles was achieved by electrospray pyrolysis (Marijnissen, TU Delft, the Netherlands). This technique has the the potential for production of particles with very narrow size distribution. Particles with various morphologies were produced at different process conditions. New materials such as metal fullerene compounds and composites as well as ceramic superconductors were also produced by conventional spray pyrolysis (Kodas, Univ. New Mexico, USA). The role of various chemical routes on the product powder characteristics during gas phase synthesis of powders was presented. Low temperature mixing of the precursor gases during titania formation may result in anatase that cannot be converted to rutile in situ (Pratsinis, Univ Cincinatti, USA). Basic studies on formation of silicon and silicon nitride particles in a laser reactor were reported (Kruis, TU Delft, the Netherlands). Among other results, it was shown that classical theory of nucleation suffices to predict the onset of silicon particle formation in thermal aerosol reactors. Laser reactors can produce a large fraction of crystalline Si_3N_4 while other conventional reactors can only produce amorphous Si₂N₄.

Particle production by laser ablation was investigated since it has important applications in film deposition and powder production for synthesis of advanced materials.

Dr. D. Boulaud (IPSN/CEA, France) showed that the particle concentration increases with laser pulse energy and pulse frequency but the mean volume diameter (MVD) of the particles remains constant. Furthermore he showed that increasing the flow rate of the carrier gas increased the particle concentration but reduced the MVD indicating that coagulation dominates particle formation and growth. In a complimentary study, (Gärtner, Phillips Aachen, Germany) showed also that increasing the carrier gas flow rate reduced the polydispersity of the product powder as determined by dynamic light scattering.

Synthesis of quantum dots and columns for new opto-electronic devices was presented since it involved generation and deposition of nanosized Ag particles onto InP substrates followed by dry plasma etching. Vertical columns as many as 10%/cm² and as small as 50 -80 nm in diameter and 120-180 nm in height have been produced by this process (Wiedensholer, Univ. Lund, Sweden). The rational design of filtration of ultrafine particles from aerosol flows was addressed by Dr. Gradon (Warshaw Tech. Univ., Poland). High temperature, in-situ coating of suspended silica fibers by nanoparticles for development of new chromatographic columns for bioseparations was presented (Pratsinis, Univ, Cincinnati, USA). The competition between coagulation and sintering of nanoparticles determines the specific surface area of the coated fibers. Dr. Schmidt-Ott (Univ. Duisburg, Germany) presented a technique for in-line characterization of magnetic particles by particle penetration through a set of 2 filters with ferromagnetic fibers. This technique allows particle sizing down to 10 nm. Depending on size, particles are super-paramagnetic or ferr(i/o)magnetic. Dr. McMurry (Univ. Minnesota) presented a new technique for making tightly collimated particle beams that can be used for particle characterization on a real time basis. Specifically, he showed that skimmers vertical to aerosol flow serve as aerodynamic lenses focusing particles of a certain size to concentrate on the centerline of the flow. Bigger or larger particles are deposited on the skimmers or the pipe walls.

A particle mass spectrometer for particle mass analysis has been developed for and applied to nanosize soot and silver particles (Roth, Univ. Duisburg, Germany). The instrument operates by following the deflection of charged particles flowing through an electric field. A comparative review for characterization of nanosized particles was given (Burtscher, ETH Zurich, Switzerland). Emphasis was given on microscopic, electrical and inertial techniques as well as photoelectric charging of particles. Examples of using these techniques included laboratory generation of metal particles as well as particle formation by volcanic activity. The latest theoretical developments and experimental results of stretching the range of dynamic light scattering (photon correlation spectroscopy) for characterization of nanosize particles were presented (Schweiger, Ruhr-Univ. Bochum). The potential of electrical (differential mobility analyzers) and inertial (hypersonic low pressure impactors) instruments for nanosize particle characterization was discussed (Fernandez de la Mora, Yale, USA). A major obstacle for reliable calibration of these instruments is the lack of standard particles between 1 and 5 nm. Ultrafine particles in the atmosphere carry charges indicative to their origin (Tammet, Tartu Univ., Estonia). Finally, the potential of aerosol reactors for commercialization was discussed (Ranade, Particle Technology Inc., USA). It was argued that there is a wide array of products with respect to price that guarantees opportunities for developing a viable industry.

The Delft University of Technology (TU Delft), the J.M. Burgers Center (Research school for fluid dynamics), the Research School Proces Technology (OSPT), the Gesellschaft fur Aerosolforschung (GAeF), the Vereniging Lucht (Dutch Air Society) and the Nederlandse Vacuum Verenigning (Netherlands Vacuum Society) sponsored the Workshop "Synthesis and Measurement of Ultrafine Particles in Gas Flows" that was held May 28-29, 1993, at the Mechanical Engineering Amphitheater, University of Technology Delft, the Netherlands.

Host was Professor Brian Scarlett while the Workshop Chair was Dr. Jan Marijnissen, both from TU Delft and the co-chair was Prof. Sotiris E. Pratsinis, University of Cincinnati, USA. The Organisation was in hands of ir. Mark A. Stoelinga. We would like to acknowledge drs. Maartje Winkel and ir. Lex Mollinger for their efforts in typing this manuscript.

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Synthesis of Ultrafine Particles



CONTROLLED PRODUCTION OF SUPERFINE PARTICLES (1 nm < d_p < 50 nm) BY AEROSOL PROCESSES

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INTRODUCTION

Superfine particles (1 nm $< d_p < 50$ nm) are of interest in the commercial production of specialty powdered materials, such as TiO₂ and carbon black (Ulrich, 1984) and optical fibres (Bautista et al., 1990), and may have unusual properties resulting from their small size (Gleiter, 1989; Ichinose et al., 1992). They are also of environmental concern since they represent the gateway to the formation of the submicron mode in coal combustion and incinerator emissions.

There are at least two routes to the synthesis of superfine particles (which are also called *primary particles*) by aerosol processes: (1) collision of small particles which sinter to form larger particles, until the temperature falls and sintering ends; and (2) condensation on nuclei formed by homogeneous nucleation or introduced into the gas. These processes may occur simultaneously. At high concentrations collision processes tend to dominate. This paper focusses on the interaction between collision and sintering processes in the growth of superfine particles.

The formation mechanisms of nanometer-sized aerosol particles are poorly understood. Particle growth by coagulation has been the subject of much study, but there have been few controlled studies of superfine particle formation. Most models of particle growth by collision and sintering treat sintering as a constant rate process (Ulrich and Subramanian, 1977), whereas it is actually a very strong function of temperature and particle size (Koch and Friedlander, 1990a; 1990b). The sensitivity of sintering rate to temperature is especially important in non-isothermal processes, such as flame reactors, because the final particle size is highly dependent on the temperature-time relationship in the reactor.

THEORY OF SUPERFINE PARTICLE GROWTH

For non-spherical particles there is a tendency to approach the state of minimum free energy, corresponding to a spherical shape. Sufficiently close to equilibrium it can be assumed that the rate of approach to equilibrium is described by a linear relationship (Koch and Friedlander, 1990a):

$$\frac{da}{dt} = -\frac{1}{\tau} \left(a - a_{sph} \right) \tag{1}$$

where τ is the sintering rate coefficient, *a* is the surface area of a particle of volume *v*, and a_{sph} is the surface area of a spherical particle of the same volume. The atom (or molecule) flux within a solid particle is (Johnson, 1969):

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$$j^{*} = -\frac{D}{\Omega kT} \nabla \mu_{a} \tag{2}$$

where μ_a is the atom (or molecule) chemical potential, D is the diffusion coefficient, Ω is the molecular volume, and k is Boltzmann's constant. It is assumed that the vacancy concentration is at equilibrium (Berrin and Johnson, 1967). In a non-spherical particle the variation of curvature around the surface produces a stress distribution, resulting in chemical potential gradients within the particle (Johnson, 1969). The local surface stress is $\sigma_s = \gamma \Gamma$, where γ is the surface tension and Γ is the local curvature. The excess chemical potential at the surface due to curvature is $\mu_{as} = \sigma_s \Omega$.

The form of the rate coefficient can be derived by dimensional analysis. The characteristic length is $v^{1/3}$, and characteristic energy per molecule $\gamma \Omega / v^{1/3}$. The number of molecules in a particle is v/Ω . Non-dimensionalizing Equation 2, the characteristic time for the sintering process is given by:

$$\tau \propto \frac{kTv}{D_{eff}\gamma\Omega} \tag{3}$$

The proportionality constant for this relationship depends on the shape of the particle. It can be considered constant for a given shape (geometric similarity). It is assumed that the proportionality constant is equal to unity.

The effective diffusion coefficient D_{eff} contains contributions from diffusion through the crystal lattice, grain boundaries and other dislocations (Le Claire and Rabinovitch, 1984). Diffusion in superfine particles is not well understood. The number of atoms in a nanometre-sized particle (~ 10³) is insufficient for properties of the bulk material to be applicable (Ichinose et al., 1992). However, it is assumed that conventional concepts of volume, grain boundary and surface diffusion can be used to describe the atom flux.

The population balance equation for the continuous size distribution function is (Koch and Friedlander, 1990a):

$$\frac{\partial n}{\partial t} + \frac{\partial n\dot{a}}{\partial a} + \frac{\partial n\dot{v}}{\partial v} = \frac{1}{2} \int_{0}^{v} \int_{0}^{a} \beta(v', v - v', a', a - a') n(v', a') n(v - v', a - a') da' dv' - n(v, a) \int_{0}^{\infty} \int_{0}^{\infty} \beta(v, v', a, a') n(v', a') da' dv'$$
(4)

The particle number concentration in a volume range between v and v + dv and an area range between a and a + da at time t is n(v,a,t), the continuous size distribution function. The collision frequency function β is assumed to be a function of volume and area only. The second term of Equation 4 represents the motion in area-space due to sintering. The third term represents the motion in volume-space due to condensation, which is assumed to be zero. The right hand side is the change due to collision. Multiplying Equation 4 by a and integrating over a and v, a rate equation for the change of the total surface area of an aerosol per unit mass of gas is obtained:

 $\frac{dA_m}{dt} \approx -\frac{1}{\tau(\overline{\nu})} \left(A_m - A_{sph} \right) \tag{5}$

This equation is approximate because the integration over v is not exact; the rate coefficient is assumed to be equal to that of the average particle size. The term A_{sph} is the total surface area of an aerosol formed by collision with complete sintering, *i.e.* the minimum possible surface area of the aerosol. This is a basic assumption in the classical theory of coagulation. The diameter of particles growing by coagulation in the free molecule regime in a gas cooling at a constant rate, i.e. $T = T_o - \kappa t$ where T_o is the initial (maximum) temperature and κ is the cooling rate, is:

$$\overline{d}_{p,sph} = c_{FM} V_m^{2/5} \left(1 - \sqrt{\frac{T}{T_o}} \right)^{2/5}$$
(6)

where:

$$c_{FM} = \left[\frac{5a_{FM}\rho_{go}T_{o}}{6\kappa} \left(\frac{6}{\pi}\right)^{5/6} \left(\frac{6kT_{o}}{\rho_{p}}\right)^{1/2} \left(\frac{3}{4\pi}\right)^{1/6}\right]^{2/5}$$
(7)

and V_m is the volume of particle material per unit mass of gas, a_{FM} is a dimensionless constant equal to 6.55, ρ_p is the density of the particle material, and ρ_{go} is the gas density at T_o .

The average diameter of non-spherical particles is defined in terms of the volume loading and the total surface area:

$$\bar{d}_p = \frac{6V_m}{A_m} \tag{8}$$

Diffusion is a thermally activated process and the diffusion coefficient can be represented by an expression of Arrhenius form:

$$D(T) = D^{o} \exp\left(\frac{-E_{act}}{kT}\right)$$
(9)

where E_{act} is the activation energy. The analysis is simplified by introducing a characteristic diameter d_{pc} (Koch and Friedlander, 1990b), which is defined in terms of the cooling rate κ and material properties at T_{a} :

$$\tau(d_{pc}, T_o) = \frac{T_o}{\kappa} \tag{10}$$

Temperature and diameter are non-dimensionalized by T_o and d_{pc} : $\tilde{T} = T/T_o$ and $\tilde{d}_p = d_p/d_{pc}$. The dimensionless activation energy is defined $\epsilon = E_{ac}/kT_o$. For purposes of this analysis it is assumed that a single activation energy is representative of the diffusion process. Changing the independent variable of Equation 5 to temperature, non-dimensionalising, and substituting Equations 3, 6 and 8-10 with either D_v or $D_{gb}b/d_p$ for volume diffusion or grain boundary diffusion respectively, we obtain a differential equation describing solid particle growth at a constant cooling rate in the free molecule regime:

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$$\frac{d(\tilde{d}_p)}{d\tilde{T}} = \frac{1}{\tilde{T}\tilde{d}_p^{m}} \exp\left(\epsilon - \frac{\epsilon}{\tilde{T}}\right) \left[\frac{\alpha \tilde{d}_p}{\left(1 - \sqrt{\tilde{T}}\right)^{2/5}} - 1\right]$$
(11)

where:

$$\alpha = \frac{d_{pc}}{c_{FM} V_m^{2/5}} \tag{12}$$

The exponent *m* is equal to 2 for volume diffusion and 3 for grain boundary diffusion. The initial conditions are $\tilde{T}_o = 1$ and $\tilde{d}_{po} = 0$. The equation for the growth of liquid droplets is slightly different:

$$\frac{d(\tilde{d}_p)}{d\tilde{T}} = \exp\left(\epsilon - \frac{\epsilon}{\tilde{T}}\right) \left[\frac{\alpha \tilde{d}_p}{\left(1 - \sqrt{\tilde{T}}\right)^{2/5}} - 1\right]$$
(13)

with a rate coefficient for sintering by viscous flow defined as $\tau \propto \mu d_p / \gamma$ (Koch and Friedlander, 1990a). The viscosity μ is described by an Arrhenius expression.

The relative rate of sintering to collision decreases rapidly with temperature. The dimensionless group α compares the characteristic sintering diameter with the characteristic collision diameter (Figure 1). As $\alpha \rightarrow 0$, particle growth is sintering-limited, leading to small superfine particles. Equation 6 was derived assuming that the growth rate is independent of the initial homogeneous nucleation burst, but this assumption becomes less valid as the value of α approaches zero because particles approach the size of the original nucleation nuclei. As $\alpha \rightarrow \infty$, sintering occurs instantaneously, and particle growth is collision-limited, corresponding to the classical coagulation theory for instantaneous coalescence (Equation 6). The useful range of Equations 11 and 13 is in the intermediate regime of α .



Figure 1: The dimensionless parameter α indicates the dominant growth mechanism. As $\alpha \to \infty$, sintering is rapid and growth is collision-limited. As $\alpha \to 0$, sintering is slow compared with the collision rate.

Dimensionless diameter d_p rapidly approaches an asymptotic value d_{ph} because sintering becomes very slow as temperature decreases. The solutions of Equations 11 and 13 are independent of the upper integration limit (final temperature), as long as the final temperature is not too close to the initial temperature. In the collision limit ($\alpha \rightarrow \infty$) particle diameter approaches an asymptote more slowly. Figure 2 shows solutions of Equations 11 and 13 as functions of the dimensionless parameters α and ϵ . The value of d_{pf} is independent of α when growth is sintering-limited.

There are three basic process parameters in the collision-sintering theory: the maximum temperature T_o , cooling rate κ and aerosol volume loading V_m . A parametric analysis of these quantities is shown in Figure 3 for the growth of silica by viscous flow. Values of α are less than 100; processes in which α is large are more easily analyzed using classical coagulation theory. Particle growth is completed before the temperature decreases below the melting temperature, so it is assumed that silica is liquid.

The qualitative effects of each process condition are summarized in Table 1. The table applies to conditions which are typical of flame processes. Volume loading only influences the collision rate, and becomes important when growth is collision-limited. The effect of cooling rate is small when growth is sintering-limited or in volume and grain boundary diffusion, and becomes more important in viscous flow or when growth is collision-limited. Particle growth is most sensitive to the maximum gas temperature when $\alpha \sim 1$. The effects of T_o become less important as α approaches its limits. As $\alpha \rightarrow 0$, changes in T_o result in a moderate increase in sintering rate, and as $\alpha \rightarrow \infty$, temperature influences only the collision rate.



Figure 2: Asymptotic solutions of Equations 11 and 13.

COMPARISON OF THEORY WITH EXPERIMENTAL RESULTS

The effects of process conditions were investigated by generating alumina particles in a turbulent free jet within a methane/air flame (Windeler, 1992). The particles were produced by oxidation of trimethylaluminum (TMA) vapor, which reacts spontaneously in oxygen. Particle size was controlled by varying the jet velocity (and hence the temperature profile) and the concentration of reactants in the jet.

Particles produced in the jet were mainly spheroidal, although oblong spheroids or egg shapes were also observed. Particle sizes are listed in Table 2. Within the measurement uncertainty (\pm 0.3 nm), particles were monodisperse. Larger particles were generated at lower jet velocities because of the higher maximum temperatures. The 2.2 nm particles were more elongated than the larger particles, indicating that the high surface-to-volume ratio may increase the importance of surface diffusion. Electron diffraction patterns showed that the particles were amorphous. The aerosol volume loading was varied between 1.0×10^{-9} and 1.0×10^{-8} m³ Al₂O₃/kg gas by controlling by the flowrate of TMA, but the particle size was not influenced by loading.

The range of particle sizes that were produced was limited by experimental constraints. Larger particles were not produced because the flame temperature could not be increased. Lower temperatures were obtained by increasing the jet velocity, but discrete particles were not formed at jet velocities above 4000 cm/s. Instead, the alumina formed shapeless amorphous mounds.



Figure 3: Parametric analysis of the effects of cooling rate, maximum temperature and volume loading on the growth of silica particles in a flame process.

Calculations were made for the growth of solid alumina particles assuming grain boundary and volume diffusion mechanisms. The diffusion data were obtained from studies of the sintering of powder compacts of coarse particles (Cannon et al., 1980). The effect of mixing of the jet with surrounding gas was taken into account by the expression $V_m \approx V_{mo}T/T_o$ (Delattre and Friedlander, 1978). Although the melting temperature of nanometre-sized particles is lower than the bulk melting point (Peppiatt and Sambles, 1975), estimates indicate that under experimental conditions the particles were formed in the solid phase. The calculated primary particle diameters (Table 2) were much smaller than the measured values. It is likely that surface diffusion, which is not explicitly taken into account in Equation 11, also plays an important role (Prochazka and Coble, 1970). The maximum possible diameters calculated using Equation 6 were much greater than the experimental diameters, indicating that the influence of the sintering rate is significant.

Parameter	$\alpha \rightarrow 0$	$\alpha \sim 1$	$\alpha \rightarrow \infty$
ĸ	small	small (moderate for viscous flow)	moderate
T_o	moderate	large	moderate
V_m	small	moderate	large

 Table 1: Relative influences of process parameters on particle growth, based on conditions typical of flame processes.

Maximum temperature	Cooling rate (K/s)	Jet velocity (m/s)	Experimental particle diameter (nm)	Predicted diameter (nm)	
(K)				Grain boundary diffusion	Volume diffusion
1140	710	4.3	4.4	.36	10-4
1010	820	12.7	3.2	.085	10-5
890	1080	21.2	2.2	.015	10-6

Table 2: Experimental and predicted alumina particle diameters.

The discrepancy between experimental results and predictions is probably due to the inadequacy of existing sintering theories, and the lack of diffusion data for nanometer-sized particles. The few published studies of diffusion of sub-micrometer alumina particles are concerned with particles at least an order of magnitude larger than those in this work. Vergnon *et al.* (1970) measured the initial stage of sintering of polydisperse δ -alumina particles (16 nm $< d_p < 120$ nm) at temperatures between 1320 K and 1670 K. They found that the shrinkage rate was not consistent with either volume diffusion or grain boundary diffusion.

The under-prediction of particle size may indicate an enhancement of the diffusion rate in nanosized particles. Horváth *et al.* (1987) performed experiments which indicate that self-diffusion rate in compacts of nanocrystalline copper powder ($d_p = 8$ nm) is increased and the activation energy reduced compared with volume and grain boundary diffusion in the bulk material. This effect has been attributed to the large volume fraction of interfaces in nanocrystals, unrelaxed interface structure resulting in surface-like diffusion, and the high concentration of triple line junctions, which occur where three interfaces intersect. In addition, there is little data available on the sintering of isolated nanometer-sized particles (as opposed to powder compacts), which would better represent the sintering process in the aerosol.

CONCLUSIONS

Theoretical analysis shows that the final size of spheroidal nanosized particles is strongly influenced by the relative rates of sintering and collision. In a constant cooling rate process the maximum gas temperature is the most important process parameter, because sintering is an activated process and is thus a strong function of temperature. The volume loading of aerosol material is important when growth is collision-limited. Variations in cooling rates in the range of those that occur in flame processes $(10^3 \text{ K/s} < \kappa < 10^4 \text{ K/s})$ do not significantly affect particle size except in collision-limited growth.

The size of alumina primary particles formed in a jet aerosol generator was controlled by varying process conditions. Finer particles were produced by increasing the jet velocity, which reduced the maximum temperature of the flame. Changing the loading of aerosol material in the jet had little or no effect. Primary particle size was not accurately predicted by the collision-sintering theory, probably because of poor understanding of the solid-state diffusion processes in nanometer-sized particles.

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PRODUCTION OF ZERO-DIMENSIONAL QUANTUM DOT STRUCTURES USING ULTRAFINE AEROSOL PARTICLES

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Introduction

One of the most important forces in research and industry of microelectronics is to develop components and systems to satisfy future data and signal processing, where very fast and well integrated circuits will be demanded. Very interesting in this respect are nanometer-sized structures because of their coupled optical and electrical properties. Such low dimensional structures, e. g. Quantum Well Wires (OWWs) and Quantum Dots (ODs) have strongly modified density of states, in the case of OD structures, for example, the density of states can be approximated by a delta-function. The discreteness of levels in such structures restricts the perturbations which permit transitions between the levels and thus the lifetime of an excited electron can be very long. In this case the lifetime is determined by the radiative transition rate. Apparently, these properties of low dimensional structures potentially give superior performance of optical devices based on QWWs and QDs (Weisbuch and Vinter, 1991). The usual approach to fabrication of QWWs and QDs is to use electron beam lithography and etching, by which it is possible to obtain structure sizes of about 30 - 50 nm (Merz and Petroff, 1991 and Samuelson et al., 1992). However, these techniques are slow and not suitable for production on an industrial level. We have reported the fabrication of nanometer sized columns in InP using aerosol deposition and plasma etching techniques (Wiedensohler et al., 1992), which actually show strong potential being a technique that can be extended to industrial production. In this paper we present the technology of fabrication of sub-100 nm QD structures using aerosol deposition and combined dry and wet etching. We also show how the QW thickness affects the quenching of QD luminescence.

Experimental

We present a novel technology for the fabrication of QD structures based on the deposition of ultrafine silver particles (20 to 40 nm in size) onto the surface of Ga_{0.47}In_{0.53}As/InP quantum well structures grown by metal organic vapor phase epitaxy (MOVPE). The quantum well structures consisted of 3 Quantum Wells (QW) with nominal thickness of 3, 8 and 18 monolayers (ML) with the thinnest QW being on top of the structure. A reference layer of Ga_{0.47}In_{0.53}As was grown below QWs for lattice matching control. The QWs were separated by 15 nm barriers of InP and the cladding layer was about 66 nm in thickness. Details of MOVPE growth can be found

in Seifert et al. (1990). The silver particles are produced by homogeneous nucleation with a tube furnace generator. After size-selection in a Differential Mobility Analyzer (DMA), the monodisperse particles are deposited onto the InP surface. In this work, silver particles, 40 nm in diameter, were used as an etching mask. Fig. 1 shows schematically the set-up of the aerosol generator used in the present work, with more details given in Wiedensohler et al. (1992).



Fig. 1. Schematic illustration of the aerosol deposition and plasma etching techniques used for patterning of $Ga_{0.47}In_{0.53}As/InP$ quantum well MOVPE structures. Silver particles are produced by a homogeneous nucleation in a flow of nitrogen. They are charged in a bipolar charger and size-selected in a Differential Mobility Analyzer giving a narrow size distribution. Aerosol particles are then deposited onto the InP-based structure which is etched subsequently in a low-energy ECR-plasma.

Results and discussion

The silver particles (20-40 nm) produced by a nucleation/condensation aerosol generator (Scheibel et al., 1983) and size-selected with DMA consist mainly of agglomerated, primary particles smaller than 10 nm in size. Transmission Electron Microscopy (TEM) images show that the shape of particle becomes more non-spherical the larger the size of the DMA-selected particle is. Fig. 2 shows a 20 nm silver particle formed by agglomeration of mono-crystalline primary particles.

The silver particles act as a mask for CH₄/H₂/Ar Electron Cyclotron Resonance (ECR) plasma etching at low bias energy (about 100eV), a process which is optimised for the formation of columns 50 to 100 nm in diameter and 120 to 280 nm in height with a surface density of about 5.10^8 cm⁻². Their size and stability were found to be dependent on the etching conditions, especially methane concentration and ion energy. We believe that the silver particles act as nucleation sites for the formation of polymeric film around them resulting in highly selective etching.

Polymerisation strongly depends on methane concentration and particle size which is illustrated in Fig. 3. Here the survival rate (SR), i.e. the ratio of produced columns to the number of deposited Ag particles is shown as the function of methane concentration and size of the particles. The reason that small particles do not survive can simply be explained by the fact that silver do not perfectly stand the argon ion bombardment. The SR smaller than 1 of larger particles (30-40 nm) is probably caused by the lower density of agglomerates compared to mono-crystalline particles.



Fig. 2: TEM image of a 20 nm silver agglomerate produced with a nucleation/condensation aerosol generator and deposited after size-selection on a thin silicon disc.



Fig. 3. Dependence of stability of aerosol Ag particles (SR-"survival rate"-ratio of density of columns produced to the density of deposited silver particles) on methane concentration in plasma. A higher stability of 30 nm particles compared to 20 nm ones is shown. Radio frequency bias voltage is given in the upper right corner of the figure.

Our experiments have shown that size of etched columns does not depend very much on the diameter of the silver particles deposited or plasma conditions, but the efficiency of column production (SR) is affected. In order to further decrease size of the columns and to remove the damaged layer, several wet etching solutions have been tested, including HBr:HNO3:H2O (1:1:30 at 20 °C), HCl:HNO3:H2O (1:2:4 at 40 °C)(Jacobs et al., 1992) and HCl:H₂O (1:1 at 4 °C). The two first solutions are non-selective, etching both InP and GaInAs at the etching rate of about 5 nm/s, while concentrated HCl was reported to etch InP without affecting GaInAs (Temkin et al., 1988). The wet chemical etching step was performed while stirring the solution after in situ removal of the polymer depositions in an oxygen ECR plasma. It was found, however that the HBrbased etchant had a tendency to produce a residue around the columns. Moreover, all three solutions showed significant decrease of etching rate after a first wet etching so subsequent etching steps resulted in negligible changes in shapes of the columns, unless the etching time was increased to 20 s or more. This indicates the formation of a passivating layer after wet etching. Nevertheless it was possible to fabricate needle-like columns in Ga0.47In0.53As/InP QW structures with diameters as small as 30 - 40 nm in the middle of the column. Fig. 4 illustrates this by showing the columns immediately after dry etching (a) and after additional wet etching in HBr:HNO3:H2O for 2 seconds (b). Note a significant decrease in the lateral size of the columns after wet etching.



Fig. 4. a) Large columns (~ 100 nm in diameter) in the GaInAs/InP after dry etching and oxygen stripping.



b) The same sample as in Fig. 4 a) after additional etching step in HBr:HNO3:H2O for 2 seconds.

A set of experiments was carried out in order to investigate the influence of wet etching steps on low-temperature (6K) photoluminescence (PL) of QD structures. For this purpose PL was measured at several places on the structure after each wet etching step in HCl:HNO₃:H₂O. The thinner the QW layer is the higher is the energy detected of the PL signal. Despite the difference of shape and energy of the emission peaks of QW as a function of position on the sample, especially for the top QW, the general trend

was obvious: (1) The most significant change in the PL spectra occurred after the first wet etching step. It resulted in redistribution of intensities of emission of QWs, the peak of the thinnest QW becoming the strongest one. (2) Longer wet etching led to disappearance first of the emission from thicker QWs (18 and 8 ML) and later (after 17 seconds of wet etching) the emission from the thinnest QW was almost totally quenched.

Scanning Electron Microscope investigation of the structure did not show any noticeable decrease in diameter of the columns, although a change in size of less then 10 - 15 nm, which is expected for etching in HCl:HNO₃:H₂O solution, is difficult to register due to variations of their size across the specimen. Taking into consideration the initial diameter of QDs after dry etching (70 - 100 nm in this case), one can explain quenching of luminescence using the "phonon bottleneck" theory (Benisty et al., 1991). Fig. 5 shows the typical PL spectra of the unprocessed reference sample, the QD sample after dry etching.



Fig. 5. Low-temperature photoluminescence (PL) spectra of a) unprocessed reference sample (1.22, 1.02 and 0.94 eV peaks correspond to 3, 8 and 18 ML, respectively), b) as-dry etched sample and c) dry+wet etched sample (HCI:HNO₃:H₂O, 1 second). Note the higher intensity of PL signal from the thinnest QW after wet etching step (c). Low intensity of the emission from 3 ML QW in dry etched sample b) could be a result of radiation-induced damage. Observed variation of the peaks position is due to non uniformity of QW thickness across the sample. This is supported by cathodluminescence (CL) data.

To investigate if variations of relative intensities of ML-splitting observed in the PL (Fig. 4) are significant, we have studied the sample using low-temperature CL. This study revealed that there was a thickness gradient of the QWs across the area where the PL was measured. The CL spectra were dominated by 3 ML peak (1.16 eV) at one end of the area and by 2 ML (1.22 eV) at the other (Fig. 6). Between these positions on the surface any ratio of 2 to 3 ML peak intensities can be found. The CL imaging also

showed that the luminescence signal originates from the columns and not from unintentionally produced mesas, often found in such structures. Thus the small variations in the relative intensities of ML-split peaks of each of QWs are not believed to be significant, but the strong variations intensities of emissions from QWs with different thickness are significant.



Fig. 6. CL spectra taken at positions a), b), c) separated by about 1 mm on the dry+wet etched QD sample. The positions correspond to the place where PL spectra were measured (Fig.5c). The thickness of the thinnest QW varies across the sample so that positions can be found with dominant 2 or 3 ML peaks.

Conclusions

In conclusion, we have shown the feasibility of utilisation of aerosol deposition and a combined dry and wet etching techniques for fabrication of sub-100 nm QD structures. The CL imaging confirmed that the signal comes from the QDs and not from mesas on the sample. The observed change in PL intensity from QWs with different thickness after wet etching is in agreement with the "phonon bottleneck" theory for carrier relaxation in QDs.

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Physical

Production Processes

For Nanostructured Materials

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Abstract

We present three physical production methods for the preparation of the powder necessary for the synthesis of nanostructured materials: conventional inertgas evaporation, high-pressure sputtering and inert-gas evaporation in a forced-gas flux. For each method the advantages and disadvantages are discussed. We shall emphasize the last production process, since it seems to have almost all of the positive aspects of the former two processes and since it yields major improvements with respect to powder characteristics.

1) Introduction

During recent years considerable interest has been focused on nanostructured (ns) materials made by consolidating a powder whose average particle size lies in the range 5-15 nm. Through consolidation the surfaces of the particles become part of the newly created grain boundaries and hence, for incompatibility reasons, the solid matter in the grain boundaries is in a constrained state. Thus, the density and the nearest-neighbour coordination of this state differs from the one encountered with ordinary crystals and/or glasses of the same chemical compostion. Since the properties of solids are mainly determined by the density and the nearest-neighbour coordination and since ns materials contain a high density (typically 10^{19} cm⁻³) of grain boundaries, the properties of ns materials deviate from the ones of glasses and crystals of the same chemical compostion.

Obviously, the extent of these deviations depends on the volume fraction of grain boundary present in the ns matter and, hence, on the particle size of the powder used. Thus, as in every metallurgical powder process, the properties of the final product depend crucially on the properties of the powder, i.e. the particle size. Therefore, the production method of the powder plays an important role in the synthesis of ns materials. There is a variety of production methods suitable for the powder synthesis, e.g. sol-gel methods, high-energy milling, chemical vapour deposition and physical production methods, to name but a few. In this contribution we present three examples of the latter group: conventional inert-gas evaporation, high-pressure sputtering and inert-gas evaporation in a forced-gas flow.

2) Conventional Inert-Gas Evaporation

One of the most common physical production processes for ns materials [1] is a modified inert-gas evaporation method introduced by Gleiter and co-workers about 10 years ago [2]

Figure 1 shows a schematic sketch of a production unit. It consists of a UHV chamber within which a cold finger and a resistively-heated evaporation source are placed. The material, e.g. Cu, is evaporated into an inert-gas atmosphere, e.g. 1 mbar He. Through interatomic collisions with the He atoms, the evaporated Cu atoms lose kinetic energy and condense in the form of small crystals a few nanometres across. It is commonly believed that with inert-gas evaporation the growth

proceeds by coalescence in a layer above the surface of the melt [3]. Due to the natural convection established between the hot source and the liquid- nitrogen-cooled cold finger, the particles are transported to the cold finger and accumulate there as a loose powder. After restoring high vacuum, the powder is scraped from the cold finger and funneled into a piston-and-anvil device, where it is compacted in situ.



Fig. 1: Production unit for conventional inert-gas evaporation

Although over the recent years conventional inert gas evaporation has certainly pioneered powder production for nanostructured materials, there are quite a number of problems associated with it. There is a temperature distribution across the length of the evaporation boat, resulting in different number densities of nuclei formed and hence in different growth conditions at different boat positions. Thus, the powder tends to develop a rather broad particle size distribution. Furthermore, the chamber walls and the cold finger are highly thermally loaded, leading to outgassing that in turn enhances the likelyhood of incorporating impurities in the powder. Very often one must deal with alloy formation between the material being evaporated and the crucible material. At best this leads to contamination of the powder but frequently the crucible will melt and end the experiment. Last but not least, one is reestricted evaporating relatively low-melting-point materials; metals like W or ceramics are not producible by this technique.

The latter two points are especially very difficult, if not impossible, to circumvent. Therefore, it is necessary to have an alternative production process, such as high-pressure sputtering.

3) High-Pressure Sputtering

The difference between high-pressure sputtering for the preparation of ns powders and the normally encountered sputtering as used for the synthesis of thin films is that the sputter source is now operated at pressures of approximately 0.3 to 1 mbar. We need this high pressure to obtain particles rather than thin granular films. Ideally we would like to increase the pressure still further but then the source does not work satisfactory due to plasma instabilities. Thus, we are confined to a delicate transition region and have to control the process parameters (Ar gas pressure p, power of the source L and distance between source and cold finger d) very accurately in order to obtain the desired result.

The production of nanostructured materials is virtually the same as with conventional evaporation. The evaporation source has simply been exchanged with a sputter source Depending on the choice of process parameters, there are three morphologies producible with high-pressure sputtering (Fig. 2): particles, thin granular films or a transition morphology showing features of both, i.e. particles embedded in a matrix of a thin, granular film.





Fig. 2: Morphologies produced by high-pressure sputtering: particles (a), thin, granular film (b), transition morphology (c)
We identified the thermalization of the sputtered species and the number density of nuclei formed s the two parameters important for determining the morphology [4]. One prerequisite for particle formation is that the ejected atoms must be thermalized. This means that they have to lose energy by collisions with the gas atoms until locally a high supersaturation is produced and hence nucleation is induced. The other necessary condition is that the number density of nuclei must be sufficiently high for subsequent growth to occur. Only if those two conditions are met will we produce particles with the high pressure sputtering process. In contrast, if the sputtered species are not thermalized, only atoms and subcritical clusters will hit the cold finger and a thin granular film will grow. The transition morphology occurs if either (i) only a minor part of the sputtered species is thermalized, nucleates and grows to particles or (ii) all of the ejected atoms are thermalized and nucleation takes place, but the number density of nuclei is too low for further growth to occur. This means that the cold finger is mainly hit by atoms and subcritical clusters and only a small amount of particles, resulting in a morphology of particles embedded in a thin film.

From an experimental point of view it is important to know how the process parameters, i.e. p, d and L, relate to the parameters of thermalization and number density. Because this relationship is rather complicated we refer to Ref. [4] for details. However, as a rule of thumb the following tendencies exist:

- An increase in pressure decreases the mean free path in the gas, making cooling more efficient. Hence, thermalization becomes easier to achieve and particle formation more likely. Thus, high gas pressure promotes particle formation.
- An increase in distance between the sputter source and the cold finger increases the residence time of the sputtered species in the gas atmosphere. Consequently, there is more time to cool the sputtered species. Thermalization may be accomplished, and we should obtain particles. Hence, increasing the distance makes particle formation more likely.
- In contrast, an increase in power makes thin-film formation more probable because the sputtered species have more energy, thus making thermalization much more difficult to achieve.

The sputtering process is very sensitive to changes in P, d and L, and there is only a small window in parameter space where particles are producible at all. For instance, particles are obtained only when sputtering at pressures in the range 0.3 to 1 mbar. Less than 0.3 mbar leads to thin film growth and above 1 mbar the source is difficult to run due to plasma instabilities.

In this context it is interesting to determine the particle growth mechanism. Since it is possible to infer from the particle size distribution the mechanism for growth, we have determined the distribution. For that we sputtered onto a transmission electron microscope (TEM) grid attached on the cold finger, examined it in the TEM and from the dark field image evaluated the distribution with the help of an electronic image-processing system. We found that the particle size is log-normally distributed. Following Granqvist and Buhrman's argument we concluded that also with sputtering the particles form by inert-gas condensation and that growth proceeds by coalescence. This suggests, that the nucleation and growth mechanism for particles does not depend on the production process of the condensing species.

However, high-pressure sputtering suffers from one serious drawback: it is inherently a low-rate source. It is true that increasing the sputter power or decreasing the pressure would increase the yield, but all too soon thermalization can no longer be accomplished and a thin film grows on the cold finger. Thus, high-pressure sputtering is only useful in very special cases where there is no other production process applicable.

3) Inert-Gas Evaportion in a Forced-Gas Flow

31) Convectional Problems of Conventional Inert-Gas Evaporation

In section 2 we described experimental difficulties associated with the evaporation process itself. In this section we describe two problems due to the natural convection established in the chamber.

The first is the production rate. Because of economic reasons, increasing the rate is desirable. Unfortunately, it is not possible to increase the production rate indefinitely, since doing so without simultaneously changing the convectional conditions increases dramatically the number of effusing atoms and thus the number density of nuclei, which in turn leads to more coalescence events and larger particle sizes. This means that if ns particles are to be produced, production rate must remain rather slow. The second problem is that the process suffers from low efficiency. This is due to the natural convection established between the source and any colder part of the chamber, i.e. the walls or the lid. Thus, the particles accumulate not only as they should on the cold finger but also on the walls and are irrevocably lost. Specimen production is rather time consuming since particle transport relies on the natural convection between the source and the cold finger.

Altogether, it can be said that natural convection in the chamber makes the production process uneconomic and scale up impossible. Hence, by changing the convectional conditions, for instance by applying a forced-gas flux across the evaporation source, we should be able to influence the kinetics of the nucleation and growth process with respect to a reduction of the number density and residence time of nuclei in the nucleation zone, yielding larger quantities of ns material. Furthermore, forced convection should lead to quicker transport to the cold finger and less loss to the chamber walls, i.e. higher efficiency. Forced-gas flow should also result in better powder characteristics, e.g. smaller size and narrower distributions, since the flow interferes severely with the nucleation and growth zone.

Following these considerations we modified the original experimantal (c.f. Fig. 1) set -up by mounting a nozzle above the evaporation source [5]. The nozzle was directed towards the cold finger. The system was now operated as a continuous flow system: He gas was forced through the nozzle continuously, to establish a dynamic pressure, e.g. 1 mbar, and the excess gas was pumped out via a forepump. Indeed, the efficiency could be improved since there were hardly any losses to the walls. Also the production time for one specimen was reduced by two thirds, which meant that larger quantities could be produced. However, we could no longer produce ns materials. The grain size rose to 30 nm, whereas the conventional inertgas evaporation yields approximately 15 nm. The reason for this was found to be coalescence of the powder accumulated on the cold finger due to heating by the hot gas flux.

3.2) Nanostructured Alloys Produced by Inert-Gas Evaporation in a Forced-Gas Flow

In order to hinder coalescence we turned to alloy systems [6]. Very promising systems in this respect are systems that are immiscible and exhibit grain boundary segregation, such as Cu-Bi. If the segregating component covers the crystallite surface of the other component, coalescence should be prevented.

To meet this requirement the experimental arrangement was changed as indicated in Fig. 3. Cu crystals formed above the Cu melt are blown across the Bi source, covered with Bi and finally collected on the cold finger, yielding a very small Cu grain size of approximately 7 nm.





Unfortunately, there is a major drawback to this experimental set-up. One is always confined to alloy systems behaving similarily to Cu-Bi. Thus one cannot produce pure ns-materials, since in that case coalescence on the cold finger will occur. Hence, a solution for this problem may only be achieved by a redesign of the cold finger to minimize the heat load on it thus avoiding coalescence.

3.3) Pure Nanostructured Materials Produced by Evaporation in a Forced-Gas Flow

Such a modification is sketched in Fig. 4. The collector now consists of two

liquid-nitrogen-cooled plates [7]. Crystallites of the evaporated material (Pd or Cu) are transported between the plates. Within the collector they sense the thermophoretic force, which is proportional to the temperature gradient. Since this force is perpendicular to the direction of movement of the particles, they are removed from the jet and accumulate on the inward faces of the collector. The collecting area is only minimaly thermally loaded, since it is almost not hit by the hot gas flux. The heat is rather transported towards infinity. Hence, the particles do not coalesce and we obtain very small particle sizes.



LOWER COLLECTOR PLATE

Fig. 4: Experimental set up for the production of pure ns materials by inert-gas evaporation in a forced-gas flow



Fig. 5: Bright-field TEM micrographs of powder produced in a forced flow (a) and conventionally (b)

Fig. 5 shows bright-field TEM micrographs of powder collected on TEM grids placed on the collector faces and of conventionally produced powder. Compared with conventionally produced powder the powder produced in the forced flow exhibits no habit planes but more spherical particles and a smaller particle size. From dark-field images it is possible to evaluate the particle size distribution. The result is plotted in a log-probability plot (Fig. 6).





Obviously, all points fall onto a straight line. This means that the particle size is log-normally distributed. The 50% mark of such a plot gives the median of the distribution. Compared with conventionally produced powder we found a 45% reduction of the median, i.e. 5.5 nm. Also the geometric standard deviation is slightly decreased by about 10%, i.e. 1.67. Finally, we found that the median is independent of the sampling location on the collector faces.

The occurence of the LNDF suggests that the forced-gas flux does not change the growth mechanism and that the particles also grow by coalescence. However, the gas flux seriously affects the nucleation and growth layer above the melt. It decreases the residence time and the number density of nuclei in the layer and thus yields a very small grain size and a decreased geometric standard deviation. This action also shows in the apparent lack of habit planes. In order to develop these planes a certain amount of time and sufficient coalescence partners are required. Obviously, this is no longer the case under a gas flux. This results in more spherical particles, which together with the decreased particle size lead to an improvement in powder characteristics. The independence of the median on the sampling location on the collector faces suggests that there is no further coalescence within the collector and that the particle growth region is confined to a space somewhere in front of the collector. This feature is important for the homogeneity of the powder.

4) Summary

We presented three physical production methods for the synthesis of ns materials: conventional inert-gas evaporation, high-pressure sputtering and inert-gas evaporation in a forced-gas flux.

The latter seems to be the most promising technique since it comprises almost all positive features of the first two processes and offers a number of further advantages. The action of the forced-gas flow enables larger quantities of ns material to be produced. It also increases the efficiency of the production process. This means that we can produce specimens faster and more economically. Furthermore, the gas flow improves the powder characteristics. We obtain a very small grain size, a narrower size distribution and more spherical particles. In this context it's important to remember that as far as pure ns materials are concerned, we obtain these benefits only if we use the above-described modified collector design.

Regarding the above-mentioned alloying problems we would like to note that we are currently developing a system in which we can circumvent any alloying reaction with the evaporation boat by simply evaporating the material without a crucible.

Finally, we conclude that the production process for the condensing species, i.e. conventional inert-gas evaporation, high-pressure sputtering or inert-gas evaporation in a forced-gas flux, does not have any influence on the nuclation and growth mechanism. The particle size distribution is still a LNDF, which means that growth proceeds by coalescence in a layer near the evaporation source.

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AEROSOL PRODUCTION BY LASER ABLATION

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ABSTRACT

The characterization of ultrafine particles produced by laser ablation is presented. The main parameters studied were the power and frequency of laser pulses, the flow rate and composition of the carrier gas and the nature of the target.

INTRODUCTION

The controlled production of ultrafine particles is useful in various technologies, such as catalysis, new material development and in process monitoring of impurities in metal manufacture. One way to achieve this controlled production on line, is to use laser-surface interaction, so called laser ablation (Matsumawa et al (1986), Thompson et al (1990) Shaw et al (1990)). In the present study, we emphasize on the experimental results concerning the characterization of the size distribution and the electrical charge of particles emitted during ablation of a metal target by a series of laser pulses.

The main parameters studied were the power and frequency of the laser pulses, the flow rate and composition of the carrier gas and nature of the target.

EXPERIMENTAL SET-UP

The nominal experimental set-up is shown schematically in figure 1. The ablation cell consists of a 100 cm³ volume fitted with a quartz window for passage of the laser beam. The target is installed on a plate moving in two directions continuously.

The aerosols produced are entrained by a carrier gas of different nature (argon ; nitrogen ; air) at flow rates comprised between 0.1 and 2 liters/minute.

In view of the expected aerosol concentrations, a rapid on line dilution system was needed to minimize coagulation of the aerosol at the ablation cell outlet. The dilution system consists of two stages, each of which comprises three elements : an adjustment valve to set the degree of dilution, a compressed air ejector, and a small mixing cell. The air is filtered before its return to the atmosphere. The ejector serves three purposes : supply of diluting air, suction of the gas sample through the system, and mixing of the sample with the diluting air. The air was prefiltered, dried and filtered through a very high efficiency filter. This system allows very high dilution factors up to 10.000.

A neutralizer could have been connected to the ablation cell outlet to reduce, the electrical charge distribution of particles produced, to the Boltzmann equilibrium. The aerosol instrumentation included the following devices :



<u>a condensation nucleus counter (CNC)</u> from Thermo System Incorporated (TSI), model 3020 was used, for monitoring time-dependent changes in aerosol particles concentration. This device covers the particle size range 0.01 to 2 μ m;

- an electrical aerosol analyzer (EAA) model 3030 from TSI was used. This instrument counts and sizes particles by charging them with a cloud of unipolar ions and measuring the electrical mobility distribution of the charged particles. The aerosol particle size range is determined from the charge law and comprised between 0.01 μ m to 1 μ m;
 - a differential and inertial spectrometer (SDI 2000) developed by our laboratory was used (D. BOULAUD and M. DIOURI (1988); (D. BOULAUD et al 1989). This device classifies on the basis of inertia for larger particles (> 0.3 μ m) and diffusion for smaller particles (< 0.3 μ m). In the impactor and diffusion battery particles collected on different stages and channel are weighed. The SDI operates over a wide particle size range (0.01 to 20 μ m) thus ensuring that all particles leaving the laser ablation cell are collected and classified according to size;
 - an <u>electrometer</u> from TSI, model 3068, was used. Particles bearing electrical charges are collected by a very high efficiency filter which is electrically isolated and connected to a highly sensitive electrometer which measures the current flowing from this filter. As the particles leaving the ablation cell may be positively or negatively charged, the overall charge of the aerosol is determined and not the charge distribution.

EXPERIMENTAL RESULTS

Most measurements were made using a Xe-CI laser, and some with a Nd-Yag laser. Prior to the detailed parametric study, a series of preliminary experiments was performed in order to establish the reproducibility of the experimental results and their consistency when different measurement methods were used.

Preliminary experiments

The nominal experimental conditions are defined below.

- Xe-Ci type , wavelengit . 500 mm
 energy: 75-80 mJ/pulse
- frequency: 100 Hz
- pulse duration 27 ns
- argon
- flow rate in ablation cell: 0.41/min
- copper
- shown in figure 1

A series of measurements was made under these conditions in order to assess the reproducibility of the experimental set-up. Table 1 gives the results of ten measurements. The parameters chosen were the numerical concentration, the mean volume diameter (MVD) and the geometric standard deviation of the particle size distribution, all three of which were determined from EAA measurements. The relative standard deviations of these measurements were satisfactory (20%, 7.6% and 9.6%, respectively). Moreover, these measurements were made on different

	NC (cm-3)	MVD (µm)	GSD
Mean	1.33 10 ⁹	0.123	1.59
Standard deviation	0.256 10 ⁹	0.010	0.15
Relative standard deviation (%)	20	7.5	9.6

 Table 1 :
 Reproduccibility test for 10 measurements.

 Reproduccibility test for 10 measurements.
 Reproduccibility test for 10 measurements.

	Target	MVD Argon (µm)	MVD 0 ₂ (µm)	
454 s rok reliminary v of the	Copper	0.12	Biev alleminueper	
	Nickel	0.12	0.172	
	Mobybdenum	0.15	0.211	es valacialis ^e Palicipatry es
	Tungsten	0.16	0.228	
	Aluminum	0.25	0.24	

Table 2 : MVD as a function of target metal and vector gas (flow rate = 0.75 l/min.)

antise the reproductivity of the expendience return return. Table 1 gives the results of an intrastantion is. The patenetars chosed, with the manufaction at the name of read volume the mean (ATVD) and the game of content of the designed of the antion the datable does not three of which were distributed from 6.44 measurements. The patrixen replaced devectors of distance of the content of the measurements. The address replaced devectors of distance of the content of the measurements. The address results are not distance of the second from 6.44 measurements. The address replaced devectors of distance of the second from from the measurements. The address resplaced devectors of distance of the second from from the second of the address results are made on different and 9 km. The patenet of the second second second from the second of the from address from the second second second second second second from the second secon days, and the reproducibility of the experimental set-up was therefore entirely acceptable.

Good reproducibility was also observed for the electrometer measurements since the relative standard deviation of the mean did not exceed 30 %. Under the nominal conditions, the overall electrical charge on the particles was positive, but the mean charge per particle was very low (about 3.10-4. This is equivalent to an aerosol of three positively charged particles and 9,997 neutral particles. It is important to realise that these values are indicative since the uncertainty in numerical concentrations is great, even if the measurement fluctuations remain below 10%. Given the observed values (10⁹ particles per cm³), aerosol dynamics are rapid and the numerical concentration is constantly changing: a ten-fold decrease in one second, depending on the mean diameter and standard deviation of the distribution.

The EAA results were compared with the values given by the diffusional and inertial spectrometer (SDI), which was used to determine the mass size distribution of the aerosol produced under nominal conditions.

The size distribution determined by weighing is shown in figure 2. The largest fraction (90 to 95%) of the aerosol mass was accounted for by submicronic particles, thus validating use of the EAA for the essentially real time determination of particle size distribution.

The mean mass diameter determined with the SDI was 0.343 μ m, compared with the smaller value given by the EAA (0.134 μ m). This difference is attenuated in light of the following:

the measurement range of the SDI is greater than that of the EAA, which does not take into account 5 to 10% of the supermicronic particles ;

the impactor determines the aerodynamic diameter, which is related to the geometric diameter determined by the EAA in terms of aerosol density. In light of this, the geometric diameter calculated from the SDI measurements is certainly less than 0.343 μ m. If density correction is applied to the aerosol fraction collected in the impactor (38%), a mean mass diameter of about 0.16 μ m is calculated, taking aerosol density as that of copper (Pp = 8.92 g/cm³).

Comparison with the value measured by the EAA (0.134 μm) is then entirely satisfactory.

This correction is, in fact, subject to the following uncertainties : aerosol density is not necessarily that of copper ; and if the particles are not spherical, a dynamic shape factor must be introduced.

The values of the mean volume diameter determined with the EAA are reproducible and consistent with those measured with the SDI, and doubtless correspond to a minimum value as they do not take into account the small (less than 10%) supermicronic fraction.

Parametric study

The principle of this study was to vary a single parameter at a time, starting with the nominal conditions. The influence of vector gas flow rate was studied for parameters related to vector gas, target metal.

Influence of laser pulse frequency and energy

When laser pulse frequency and energy increased, numerical concentration rose but MVD remained constant. Electrometer readings are directly related to the



Fig.3 - VARIATIONS OF VOLUMIC MEAN DIAMETER AND NUMERICAL CONCENTRATION AS FUNCTION OF CARRIER GAS FLOW RATE numerical concentration and confirmed the very low mean overall charge per particle observed in preliminary experiments.

Influence of vector gas flow rate

When vector gas flow rate increased from 0.1 to 2 l/min, numerical concentration rose from 2.108 particles/cm³ to close to 8.109 particles/cm³, and MVD decreased from 0.2 μ m to 0.08 μ m (figure 3). The mean electrical charge per particle remained low. An attempt to explain these changes in numerical concentration and MVD can be made in terms of agglomeration mechanisms. Qualitatively, the concentration is inversely proportional to residence time, or proportional to vector gas flow rate (see figure 3), thus implying that it is governed principally by agglomeration, except at the lowest flow rate.

The changes in MVD can also be explained qualitatively by agglomeration mechanisms. As the number of collisions increases with residence time, MVD will decrease with flow rate (see figure 3).Interpretation of changes in MVD with flow rate is more difficult since total aerosol volume must be constant, whatever the flow rate.

Influence of vector gas

MVD changed with both flow rate and vector gas (figure 4). Two categories of results appeared, quite clearly, linked to the presence or absence of oxygen in the vector gas.

The numerical concentrations observed were essentially the same, and the vector gas-related difference in MVD may be explained by the nature of the particles produced. In particular, the copper oxide species were of lower density, and hence for an identical mass of copper ablated, the total aerosol volume will be greater, leading to an increase in MVD. This effect was enhanced under our conditions by the fact that 1.4 times more mass was removed under air than under argon.

With air, nitrogen and argon, the mean electrical charge on the particles remained weakly positive, whereas it was weakly negative with oxygen.

Influence of target metal

Figure 5 illustrates the changes in MVD as a function of target metal. For reasons of clarity, only the curves corresponding to the nominal conditions and aluminium are shown. Other target metals are shown by points. Nickel and copper gave similar MVD values ; aluminium gave systematically higher values and Tungsten and molybdenum gave intermediate results. Concentrations corresponding to targets of aluminum, copper and nickel were quite similar, whereas tungsten and molybdenum gave lower values, particularly for the flow rate of 2 l/min.

It therefore seems difficult to provide a simple explanation for the influence of target metal on aerosol particle size distribution.

The effect on MVD of different target metal, with oxygen as vector gas was shown in table 2. The mean MVD values were determined for three or four measurements. The estimated values with argon as vector gas and an identical residence time are given for comparison.

As already observed with copper, MVD values in the presence of oxygen were higher than those seen with argon, except with aluminum where MVD was unchanged (table 2). Target-related differences were more marked with oxygen.

Qualitatively, the densities of the oxide species were always lower than the target densities, except for aluminum, in agreement with the increase in MVD seen

LASER = Xe - Cl; E = 80 mJ/pulse; F = 100 Hz Carrier gas variable nature; q = variable Target = copper



Fig.4 - VARIATIONS OF VOLUMIC MEAN DIAMETER AS FUNCTION OF FLOW RATE AND NATURE OF CARRIER GAS





Fig. 5 - VARIATIONS OF VOLUMIC MEAN DIAMETER AS FUNCTION OF CARRIER GAS FLOW RATE AND TARGET NATURE

with all targets except aluminum. The range of target densities was great (2.7 to 19.35 g/cm³), but was much reduced for the oxide species: about 4 for Al_2O_3 , 7.16 for WO₃, and 12.11 for WO₂. This is consonant with the values reported in table 2, where the range of MVD values observed with oxygen was narrower than with argon.

CONCLUSIONS

We have characterized aerosols produced during laser ablation of metals under different conditions. The main conclusions are as follows:

- reproducible results were obtained with the chosen instrumentation and experimental protocol: 10 to 30% variation, depending on the parameter measured;
- under nominal experimental conditions (see table 1), the numerical concentration of particles was about 109 cm⁻³, the mean volume diameter (MVD) 0.134 μ m, the geometric standard deviation of the distribution 1.6, and the overall mean electrical charge of about 3.10-4 was positive;
- supermicronic particles accounted for less than 10% of the total mass;
- the numerical concentration of particles increased with laser pulse energy and frequency. The MVD remained constant;
- an increase in vector gas flow rate resulted in a rise in numerical concentration of particles and a decrease in MVD. This is explained by agglomeration mechanisms, given very high particle concentrations;
- the oxidizing nature of the vector gas (air, O₂) had little effect on the concentration of particles produced, but increased MVD;
- particulate concentration and MVD depended on the target metal.

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Generation of Very Small Particles by Laser Ablation in a Carrier-gas, Deposition and Characterization

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Abstract :

Very Small Particles (= VSPs = size range 1-100 nm; also called Ultrafine Particles = UFPs) have been prepared by Laser Ablation Deposition (LAD) in quantities suited for macroscopic studies. Laser ablation of solid targets creates a plasma plume in a flowing carrier gas - e.g. consisting of Ar and oxygen in the case of oxide targets. The ultrafine particles generated are transported by the gas and are deposited on neighbouring or remote substrates. They have been characterized by TEM, BET, X-ray diffraction and dynamic light scattering. It was found that their mean diameter can be adjusted in the range of 4 to 40 nm by suitable choice of the ambient gas pressure in the range from 1 mbar to 1 bar. The maximum ablation rates obtained with about 800 Watt cw CO₂ Laser power were 1.2 g/min for SiO₂-VSPs and 0.15 g/min for Y₂O₃ VSPs.

1. Introduction :

The properties of UFPs are in the transition range from macroscopic solids to atoms/ molecules and depend on size; below 10 nm quantum size effects become dominating (here also the term "cluster" is used). There are good prospects that multicomponent solids prepared from UFPs can be tailored with new properties. In the following we will use VSPs only in connection with our own approach. Goals of this activity [1a+b, 2a, 2b] are :

- (a) Utilization of interesting and size-dependent properties of known materials.
- (b) Exploration of new properties of hitherto not available structured multicomponent VSPs (doped and/or shell-structured).
- (c) Exploitation of enhanced "solubility" in the gas phase of scarcely volatile substances in order to overcome contamination problems associated with conventional CVD.

These properties can be exploited for various applications like quantum dots, nano scale memory cells, or other microelectronic devices.

Existing generation methods [3] like e.g. wet chemical preparation suffer from disadvantages like only one-component preparation and generation rates of about 10 g / day including reaction/ processing [3,4]. Laser / electron beam cluster sources with expansion into vacuum on the other hand allow monosized clusters by mass selection, but exhibit extremely low generation rates of 1 mg/ min [3,5]. The method here [1,2], as will be described in more detail, allows size control (by choice of pressure), gas phase mixing of VSPs from different targets and simultaneous deposition, with VSP-generation rates up to 1.5 g/min per 1 kWatt of CO_2 Laser power.

Besides [5], UFP generation by Laser ablation is also described e.g. in [6,7,8]. A. Matsunawa et al. in [6] report Nd:YAG Laser ablation of metallic targets of Ni,



Dilution 0.2 ml in 2 ml H₂O ; Temperature 24.7 °C ; Viscosity 0.8966 ; Refractive index (Liquid) 1.330 ; Angle 90° ; Particle refractive index (real) 1.458 ; count rate 81.9 10 3 counts per sec ; Distance mean 172.1 nm : Standard deviation 64.4 nm ablation 20 10 . Experimental set-up for CO₂-Laser

deposition (LAD) of VSPs





Fig. 4 : TEM picture of Y2O3 VSPs at 870 mbar; 1mm = 10 nm Fig. 3 :

TEM picture of Y2O3 VSPs at 10 mbar; 1mm = 26 nm

Fig. 2 :

Malvern analysis report :

Result for size distribution of aggregates, obtained by dynamical light scattering with Malvern Zetasizer 3

Sample : SiO2; weight 0.01985 g in 2 ml H2O;

Fe, and Ti. They also found size decreases from 66 to 3 nm when reducing the pressure from 2 bar to 1 mbar. In [7] (Excimer-Laser, Cu-target) and [8] (Nd-YAG - Laser, metallic or oxidic targets, oxide UFPs), the ablation has been carried out at atmospheric pressure, with limited variability in UFP size.

2. Experimental :

The experimental set-up (fig.1) for generation of VSPs by laser ablation consists of a high power CO2-Laser Rofin-Sinar RS 700, computer controlled optics for positioning and focussing of the Laser beam, the target ablation chamber, a substrate arrangement in the flow tubing and a pump/ exhaust system. The maximum power of the CO₂-Laser is 800 Watt cw and 3,5 kW in the superpulsed mode of operation (in this case the mean power being reduced to 300 Watt). The CO₂-Laser ablation is a thermally activated process, and hence accompanied by massive heating of the target. In order to reduce thermal strains, pre-heating of the target with defocussed beam is applied. The solid targets, either porous or dense, usually oxides, are scanned during ablation, the scanning movement being effected by computer controlled translators. The gas flow of Ar, O2 or the like, provided for the ZnSe entrance window protection and particle transport, is controlled by Tylan mass flow controllers; the pressure within the chamber is held constant by means of a MKS exhaust valve control. The temperature of the target is measured by an IRCON optical pyrometer and the Laser plasma plume is optically monitored and recorded via a Philips TV camera.

In a second set-up also an Excimer-Laser has been used for investigations of "cold" ablation, but only some comparative results will be given in this context.

3. Characterization methods :

The ultrafine particles generated are transported by the gas and are collected on neighbouring or remote substrates. The deposited VSP material is characterized by <u>Transmission Electron Microscopy</u> (=TEM), determination of specific surface area (BET = <u>Brunauer, Emett & Teller method</u>), X-ray diffraction (XRD) and dynamic light scattering (DLS). No on-line characterization as in [9] was carried out, due to non-availability of commercial equipment in the pressure and size range of interest.

VSPs are either directly collected on TEM grids, which are positioned sufficiently far in the downstream region to obtain thin deposits in the monolayer range, or they are precipitated from a larger sample of VSP material after dissolving in water. They are then analysed with a Philips CM 12 TEM. The mean diameter size distribution is obtained with the aid of Image, an image analysis program e.g. available on a MacIntosh computer, after scanning the pertinent TEM-photo. By using the STEM option, also elemental composition of the particle ensemble collected can be obtained.

A second measure of mean particle size - to be more specific, of mean crystallite size D - is obtained from X-ray diffraction line widths. For evaluation the Scherrer formula [10] is used : $\beta_{1/2} = K * \lambda * 57.3 / (D \cos \theta)$



Characteristic mean VSP sizes \widetilde{d}_{VSP} obtained from TEM and BET as a function of chamber pressure for diffe-





Relationship between mean particle size \overline{d}_{VSP} (from TEM and BET) and gas velocity for SiO₂, Y₂O₃, Sc₂O₃.



Fig. 5 :

TEM picture evaluation of fig. 4. The size distribution for Y_2O_3 VSPs at 870 mbar has a mean value of 25 nm and a standard deviation of ± 11 nm.





Size distribution of of Y_2O_3 VSPs for p = 1.5 mbar: \overline{d} = 4.5 ±1.7 nm

4

Here $\beta_{1/2}$ denotes the line-width at half maximum, K is a constant in the vicinity of 1 (0.89 - 1.39), λ is the X-ray wavelength, θ is the diffraction angle and 57.3 is a conversion factor for evaluation in angular degrees. Further contributions to the line-width are lattice distortions and strain, which can be judged by a plot of $\beta_{1/2}$ * cos θ versus θ , yielding no contribution in the case of a constant value of the above product. Without that plot, D gives only a lower limit for the mean value of the particles.

The third measure for particle sizing used here is the "mean projected diameter" d obtained from BET measurements [11] of the specific surface area S : It holds $d = K / (\rho * S)$, where K is a form factor, K = 6 for spheres (K = 10 for SiO₂, used in the evaluation), and ρ is the density of the particle material. Mini-

mum amount of sample mass needed was 0.05 g. A further characterization method used was dynamic light scattering (DLS) [12], also called photon-correlation spectroscopy (PCS). In this case a part of the collected VSP material is diluted in a sample volume of water and is first treated by ultrasound for reduction of agglomeration. The light of a HeNe Laser is scattered by the particles in the suspension and the intensity pattern is registrated by a photo-multiplier. By correlating the time- changes of the pattern, an auto-correlation function is obtained. Typical fluctuation times for submicron particles in a water suspension are in the order of 1 µsec for small (3 nm) and 1 msec for large particles (300 nm). From the decay time of the auto-correlation function, the diffusion constant and hence the hydrodynamic radius in the case of monodisperse particles can be obtained. For polydisperse and multimodal samples, the decay is not linear in logarithmic scale, but can be written as a polynomial series expansion, the linear term giving the mean diffusion constant and the higher terms, i.e. guadratic term, giving a measure for the width of the distribution. Some of the limitations are, that spherical form of the particles is assumed and also, that it cannot be used if thermal convection is dominant in the polydisperse case. The measurements were carried out with a Malvern Zetasizer 3, which has a sensitivity range from 3 nm to 3µm, a typical result with a mean size of the hydrodynamic radius of 138 nm is given in Fig. 2. However it turned out by comparison with TEM, BET and XRD, that the mean size of the aggregates was determined, and not the size of the constituent particles!

4. Results:

An investigation of the relevant LAD parameters was carried out, using the first three methods described above for VSP characterization. Typical TEM pictures are shown in figs. 3 and 4 and results of TEM picture evaluations in figs. 5 and 6. In fig. 5 the distribution obtained for Y_2O_3 at 870 mbar is depicted, exhibiting a mean value of 25 nm for the mean cross section diameter and a standard deviation of 11 nm. At 1.5 mbar a size distribution of 4.5 ±1.7 nm of Y_2O_3 VSPs was achieved (fig.6). The relative width of the distribution, typically in the region 40%, can be decreased by using higher gas velocities. Similar to [6] for metal UFPs, the pressure p in the ablation chamber turned out to be the size-determining parameter. Fig. 7 shows the characteristic mean VSP sizes d_{VSP} obtained from TEM and BET (the



4 XRD spectra of Y_2O_3 VSPs, as prepared (p = 1.5 mbar) and after three subsequent heating cycles (0.5 h each) at 600°C, 800°C and 1000°C. The corresponding TEM and <u>BET results</u> have been added for completeness.







interpretation being a bit dependent on the method) as a function of chamber pressure. A decrease of d_{VSP} from about 40 nm at 1 bar to about 4 nm at 1mbar is observed for different oxides, namely SiO₂, Y₂O₃, Sc₂O₃ and also Al₂O₃ (not shown). In fig. 8 also the relationship between mean particle size and gas velocity is shown, which will be discussed at the end of this chapter. It can be seen that TEM and BET agree quite well, also with XRD (see below). A XRD spectrum is shown in fig. 9. This XRD spectrum belongs to a hitherto unknown "high temperature" phase of Y₂O₃ (very similar to the corresponding Gd₂O₃ phase). In several experiments a superposition of this spectrum with the known Y₂O₃ spectrum was found (fig.10), which can of course be an obstacle for a well-defined VSP preparation. Therefore also heating experiments for studying grain-growth and improving grain structure heating cycles at 600°C, 800°C and 1000°C, where the corresponding TEM and BET results have been added for completeness. Here only grain growth of the known Y₂O₃ phase can be observed.

The total Laser power P_L in contrast has no significant influence on mean size, yet there are indications of effects on the substructure. Of course the mass ablation rate increases with power P_L (fig. 12). The maximum ablation rates obtainable with about 800 Watt cw CO₂ Laser power were 1.2 g/min for SiO₂-VSPs, 0.15 g/min for Y₂O₃, 0.13 g/min for Al₂O₃ and 0.12 g/min for Sc₂O₃ VSPs.

The efficiency of LAD is defined by the mass- ratio of collected VSP material to the total ablated mass. Fig. 13 shows that the efficiency rises with increasing ablation rate. This can be explained by enhanced agglomeration and hence higher particulate inertia and faster wall contact. Depending on the parameters and on the arrangement, collection efficiencies between 16 and 97 % were obtained. A graph of the deposited mass profile in the downstream direction z (z=0: position of target center) is depicted in fig. 14 for arrangement (α) (fig. 1) and also normalized profiles of mass per unit length in mg / 10cm for arrangements (α) and (β). Profile (β) was obtained with a three stage cascade impactor [13], the first stage starting at z =30 cm on the exhaust side, yielding an overall 96% deposition efficiency. As to the mass collected per obstacle plate, the last stage, being designed for the mass/ size range around 30 nm, was the most effective one. This experiment was carried out with Al_2O_3 VSPs generated at p = 5.3 mbar. The important feature of all these profiles is, that the major part of the VSP material is deposited on the first 25 cm in the flow direction. The efficiency can be optimized by the use of several substrate obstacles adequately arranged in this region.

Another important question is the stability of the generated VSPs when exposed to air. By subsequent weighing of the VSP covered samples it was discovered, that the VSP material experienced a weight gain of up to 22% within 20 min. This could be traced to water adsorption. For quantitative desorption, heating up to 600 °C is necessary, which was determined by the aid of DSC (= Differential Scanning Calorimetry). To avoid water adsorption, the VSP material should either be handled in inert dry atmosphere or should be coated / imbedded in a solid matrix.

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Ablation rates of ceramics from Lamba Industrial No. 5 (1989) and for Y_2O_3 and Al_2O_3 -VSPs (PFLA) in μ m per pulse as a function of energy density in Jcm².



The efficiency E (E = ratio of collected VSP mass to total ablated mass) of LAD versus target ablation rate.

Fig. 14 :

A graph of deposited mass profile in the downstream direction z (z= 0 : position of target center) for arran-∆ G_i [mg] gement (α), also with normalized profile for arrange-∆ Gi 10 cm ment (α) and (β) of mass per unit length in mg / 10cm; in (a) [mg] (β) a three stage cascade impactor was used. No. 19 A Gi E = 45.5 % ΔG_i = mass in mg collected on inner cylinder / other substrate i 60 (a) ΔG_i / 10 cm = normalized mass in mg / 10 cm collected on inner cylinder / other substrate i per length in z-direction 40 ∆ G; / 10 cm No. 19 20 E = 96 % , with 3 stage cascade impactor No. 17 z [cm] 0 0 direction to pump 20 40 60 80

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Of course the dependence of particle size on pressure reflects the average sojourn time of the evaporated material in front of the target in the plasma plume, which will lead to larger particles the slower they leave this region. In fig. 8 the relationship between mean particle size and gas velocity has already been shown, where a velocity of 80 cm/ sec corresponds to a time of 12.5 msec for passage of 1 cm, which is typical for plasma plume extension. At higher gas velocities only a neglegible influence on size can be seen, which may be also related to the fact, that the stagnant laver thickness (laminar viscous flow!) becomes insensitive to further velocity increase (compare [14]), but expands at lower velocities. Similar to collection (fig. 14), also in this case one has to take into account that ultrafine particles diffuse farther than expected from Brownian motion, since the diffusion coefficient D_o is dependent on particle Knudsen number $2\lambda / d_p$ via the Cunningham factor C [15] (d_p = particle diameter, λ = mean free path of gas molecules). A good approximation for C in the range $2\lambda / d_p > 2.6$ (molecular movement) is C = 3.33 λ / d_p [15], leading to $D_p = k T^* 3.33 \lambda / (3 \pi \eta d_p^2)$. E.g. for Ar at p = 1 mb and $d_p = 20$ nm we obtain C = 44.6 ! These are some of the prerequisites for a future theoretical description.

5. Excimer Laser ablation and first results :

In a second set-up also an KrF-Excimer-Laser with a wavelength of 248 nm and an average power \leq 60 Watt has been used for investigations of "cold" ablation from rotating solid oxide targets. The LAD chamber arrangement is shown in fig. 15, using a gas jet from a nozzle traversing the plasma plume and hitting the substrate below for particle deposition. Target ablation rates for Y₂O₃ and Al₂O₃ of 0.1 µm per pulse were obtained for about 7 Jcm⁻² (fig.16). A pressure dependence of Y₂O₃ particle size was also observed, yielding about 30 nm at 100 mbar and 2 - 4 nm at 5 mbar.

6. Conclusions :

The Laser ablation method described here offers several advantages for the preparation of nanostructured material: It allows control of mean VSP size by suitable choice of pressure in the atmospheric to pre-vacuum range, it allows gas phase mixing of VSPs from different targets and simultaneous deposition - eventually together with CVD-layers-, with high VSP-generation rates of up to 1.5 g/min per 1 kWatt of CO₂ Laser power. The deposition efficiencies will be further improved by changes in the geometry of the gas flow system.

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Generation of submicron aerosols in a free turbulent jet.

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1 Introduction

In this note we report on studies on the formation of ultrafine aerosols with controlled properties in a free jet. Numerous papers have been written on aerosol formation in jets using turbulent jets (Amelin, 1948, Hidy and Friedlander, 1964, Sutugin and Fuchs, 1967, Sutugin et al., (1984), Strum and Toor (1992)) as well as using laminar jets (Brock et al., 1986). These studies focussed on measuring and modeling homogeneous nucleation and/or condensational growth. Hot condensible vapors (organic liquids, liquid metals, water etc.) issued through a round nozzle into a cold gas (mostly air). The vapor concentration and the temperature of the jet and the surrounding gas were such that aerosol formation and growth was controlled by the mixing process and the thermodynamic properties of the vapor as well as the material properties of the condensed phase.

The motivation of our study was to design a simple generation system producing ultrafine aerosols at very high and adjustable particle current as well as controllable particle size. The design idea was to form a dense cloud of embryos by homogeneous nucleation and to grow the particles by coagulation. We used a turbulent jet because it is technically simple, there are no wall problems and the growth process can be quenched easily at different stages. The parameters of our process are set in a way that aerosol formation is determined only by turbulent mixing and collision kinetics i.e. purely mechanical properties of the jet and the aerosol particles.

We looked at two systems: 1) A hot vapor of DEHS (di-ethyl-hexyl-sebacate) which nucleates upon mixing with cold air and forms liquid droplets; 2) TiCl₄ which reacts very fast when mixed with water vapor to form (hydrated) TiO₂ particles and subsequently solid agglomerates. Homogeneous nucleation either caused by cooling (system 1) or by chemical reaction (system 2) is the dominant gas to particle conversion mechanism. It is completed within a small distance close to the nozzle. The

subsequent particle growth is determined by (Brownian) particle collisions.

The total particle flux, \dot{N} , through a plane at a distance, x, large compared to the nozzle diameter is therefore determined mainly by the effective collison time (i.e. the exit velocity, u_0). For the average particle volume, v, the initial mass concentration, c_m , of the condensed material is a second controlling parameter. Generally, the particle size distribution function in the jet is a function of the axial and radial coordinate: x, r. The average particle volume, v, is defined as volume fraction Vdevided by number concentration N. Since these two moments of the distribution should have similar radial profiles, it is assumed that v is only a function of x. It is shown by Delattre and Friedlander (1978) and Koch et al. (1993) that the following scaling relation holds:

$$v \sim \left(\frac{c_m x}{u_0}\right)^z \tag{1}$$

where z is the so called dynamic exponent. It is related to the degree of homogeneity, ν , of the collision kernel via

$$z = \frac{1}{1 - \nu}.\tag{2}$$

 ν is zero for continuum regime coagulation whereas for free molecular growth it is related to the fractal dimension, D_f , of the particles by

$$\nu = \frac{2}{D_f} - \frac{1}{2}$$
(3)

which reduces to $\nu = 1/6$ for liquid particles with $D_f = 3$.

The relation 1 is used to design the generation system that had to meet the following requirements: number flux adjustable between 10^{10} and 10^{12} particles per second and particle size adjustable between 10 and 300 nm. The next section covers a short description of the experimental set-up. The final part of the note deals with the presentation of experimental results and their interpretation.

2 Experimental set-up

The experimental set-up is shown in Fig. 1. The aerosol precursor materials (hot DEHS vapor, TiCl₄ vapor) are issued together with the nitrogen carrier gas through a circular nozzle (flow rate Q_g , nozle diameter d) into a slowly conflowing stream of cold and humidified air. For the DEHS system the nozzle was heated to about 270°C to prevent condensation of vapor at the nozzle walls. The TiCl₄ was at room temperature. For this system, a small concentric flow of nitrogen was added to avoid build up of solid material at the nozzle edges. The mass flux \dot{m}_l of the precursor substances was established: 1) by feeding liquid DEHS into a nebulizer and evaporating the droplets in a heated tube; 2) by passing an adjustable side stream of the carrier gas through a bubbler containing liquid TiCl4. Carrier gas flow rate and mass flux of the precursor material could be set independently. The carrier gas flow rate covered the range between 1 and 10 l/min. DEHS was fed at a rate between 5 and 80 ml/h, TiCl₄ at considerably lower rates corresponding to equivalent TiO₂ fluxes between 0.001 and 0.01 ccm/h. This was obtained from the flow rate through the bubbler assuming saturation with TiCl₄. We further assumed a material density of 4 g/cm³ for TiO2. Nozzles of various sizes between 2 and 5 mm were used. The conflowing air stream was $Q_d = 500$ l/min. The air was introduced via a perforated metal plate (diameter 200 mm). The diameter of the coagulation tube was large enough so that the jet did not touch the walls. The aerosol leaves the tube through a 40 mm wide outlet where it is mixed with the rest of the dilution air that is not incorporated in the jet. The output aerosol thus represents the aerosol flowing through the plane at x = L. The number current at x = L can therefore be determined by measuring the concentration N_o in the outlet tube:

$$\dot{N} = \frac{N_o}{Q_d + Q_g} \approx \frac{N_o}{Q_d} \qquad (Q_g \ll Q_d).$$
(4)

Number concentrations were measured with a TSI model 3025 ultrafine particle counter. Size distribution measurements were done with a scanning mobility spectrometer.



DEHS, TICI4 in N2

Fig. 1: Schematics of the aerosol formation in the free turbulent jet. The important aspect in our system is that the nucleation regime is confined to a section close to the nozzle and that the aerosol properties far downstream from the nozzle are determined by collision kinetics.

3 Results and Discussion

The parameters determining number current and particle size are the two flow rates: \dot{m}_l and Q_g , and the nozzle diameter, d. Using $c_m = \dot{m}_l/Q_g$ and $\dot{N} \sim \dot{m}_l/v$ we obtain from 1 the scaling relations:

$$\dot{N} \sim \dot{m}_l^{1-z} \left(\frac{Q_g}{d}\right)^{2z} \qquad v \sim \left(\frac{\dot{m}_l d^2}{Q_g^2}\right)^z.$$
 (5)

These relations together with the respective value of the exponent are strictly valid only in the continuum (z = 1) and in the free molecular regime (z = 1.2). However they can also be used as a sectional approximation (with the proper value of z in each section) to describe the growth in the transition regime.

A first conclusion drawn from Eqn. 5 is that the number current produced by the generation system is rather insensitive to variations of the mass flux (values of z are close to one) but can be adjusted by the carrier gas flow rate and the nozzle diameter. Fig. 2 shows the the correlation for the liquid DEHS aerosol. The number current data are plotted versus Q_g for a fixed nozzle diameter (2a), respectively versus Q_g/d in 2b. They can be well approximated by a straight line. The range of the achievable number currents covers one and a half orders of magnitude in our system. The data seem to support the underlying assumption of coagulation controlled growth. The dynamic exponent, z, calculated for example from the slope of the straight line in Fig. 2a has a value of 0.88. This is significantly lower as would be expected in the continuum regime (z = 1) or the free molecular regime (z = 1.2). The average particle sizes corresponding to the number current data in 2a fall in neither of the limiting regimes but are confined to a relatively narrow range (from 0.1 to 0.23 μ m) in the transition regime. In this small intervall, the collision frequency function can also be approximated by a power law: $K \sim v^{\nu}$, where ν is negative and according to Eqn. 2, z is smaller than one.



Fig. 2: The correlation between the logarithm of the number current and the logarithm of the carrier gas flow rate gives a straight line (2a). The slope is determined by the collision kinetics in the transition regime. After normalization, the data for different nozzle diameters collaps into a single curve (2b).



Fig. 3: The number current of the TiO_2 aerosol is significantly lower than that of the DEHS aerosol which can be explained by the agglomerated structure of the TiO_2 particles.

Fig. 4: The modal mobility diameter can be adjusted over a wide range from 13 nm to 350 nm.

For the TiO₂ aerosol the same correlations hold. However, the number currents are significantly lower than those of the DEHS aerosol. This is shown in Fig 3 where the number current data for a 3 mm nozzle are plotted. The DEHS and TiO₂ flux was 15 ml/h and $5*10^{-3}$ ml/h, respectively. The difference in number current cannot be explained by the difference in mass flux of the two aerosol systems. It may be due to the fact that solid agglomerates are formed in the case of the TiO₂. Since agglomerates grow faster than spherical particles their number concentration decreases faster and the number current is lower than for the spherical particles. Furthermore, the straight line fitted to the TiO₂ data has a steeper slope in this example. A value of z = 1.08 is obtained. This is the expected trend since the TiO₂ particle sizes corresponding to the number current and the mass flux are smaller than 60 nm and particle growth is almost confined to the free molecular regime. It has to be mentioned, however, that for the TiO₂ system we sometimes obtained significantly smaller slopes as low as z = 0.68 while the correlation coefficient was still virtually equal to one.

Fig. 4 shows the geometric mean mobility diameter of the size distributions as a function of $\dot{m}_l d^2/Q_g^2$. Titanium particles could be generated in the range between 13 nm and 150 nm. The DEHS droplets were larger than 80 nm and extended up to 350 nm. The data points show the same trend as the number current data (alltough with a larger scatter). The smaller particles grow faster than those in the transition regime. The gap between the DEHS and the TiO₂ data could again be explained by the morphological differences between the two types of aerosols. The geometric standard deviation of the distribution varied between the 1.36 and 1.6 with the trend that the TiO₂ distributions had generally a larger standard deviation ($\sigma_g > 1.41$). Electronmicrographs of the TiO₂ particles are shown in Fig. 5 for a low volume flux of TiO₂ of 5*10⁻³ ml/h and a high flux 2.5*10⁻¹ ml/h). The total flow through the nozzle was 6 l/min.



Fig. 5: Electronmicrographs of TiO₂ particles for low mass concentration (a) and high mass concentration (b) of aerosol precursor material. The length of the bar is 1 μ m.

From the preceding discussion we can conclude that the aerosol properties of the two systems under investigation are determined by aerosol mechanical mechanisms, independent of the details of the underlying gas to particle conversion process. Under these conditions, the turbulent jet technique is a simple and attractive way to generate large quantitites of aerosols with controlled properties. Since the aerosol growth is coagulation controlled, the size distribution is however rather broad. A further, not vet completely evaluated, aspect of this study is the possibility to measure properties of the coagulation process. This is particularly interesting in the case of agglomerate formation because the coagulation kinetics is not completely understood. The particle size of the final output aerosol is primarily determined by the mass flux of the aerosol precursor material. Variations of the nozzle exit velocity i.e. carrier gas flow rate cause only small relative changes in the number current. From the relationship between the carrier gas flow rate and the number current one can therefore determine the 'local' degree of homogeneity of the collision frequency function. The preliminary results for TiO2 allow however no firm conclusions yet. This aspect is subject of further research on the TiO₂ system.

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Nanophase Particle Formation: Fullerenes and Multicomponent Materials

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ABSTRACT

Gas-phase synthesis and processing of nanophase materials can be accomplished by both gasto-particle conversion and spray routes. We have investigated the use of spray processes and vapor condensation for the generation of nanophase ceramic materials including hightemperature superconductors, pure fullerenes and their composites with metals. Nanophase particles (grain size~ 10 nm) of fullerenes were produced by spray drying their solution in toluene. Fullerene nanoparticles (30-40 nm) were also generated via vapor condensation under nitrogen. Fullerene-rhodium nanocomposites having a grain size of 3-5 nm for rhodium were synthesized by spray pyrolysis of a solution of mixed fullerene extract (C₆₀, C₇₀) and [(1,5-COD)RhCl]₂ in toluene. Similarly, ultrafine-grained Ag-(Bi, Pb)-Sr-Ca-Cu-O powders were obtained by spray pyrolysis of nitrate solutions. During spray pyrolysis, the grain sizes were kept small by operating at temperatures which were high enough for the complete reaction of the precursors but low enough to avoid grain growth in each particle. The chemistry and aerosol dynamics of particle formation and characterization of the product powders by a variety of techniques are described.

INTRODUCTION

Over the past decade, there has been a growing interest in the synthesis and properties of nanophase or nanocrystalline materials which are essentially assemblies of atomic clusters (1-25 nm in size) into bulk materials [1, 2]. At a nanophase level, materials have a large volume fraction of atoms at the grain boundaries. As a result of such a microstructure, a nanophase material possesses many interesting and potentially useful physical and chemical properties such as enhanced processing behaviour (sinterability) and ductility, extensive plastic

deformation, high atomic diffusivities and unique optical, electrical and chemical properties [1-3]. Gas-phase synthesis and processing of nanophase materials can be accomplished by both gas-to-particle and spray routes. So far, the synthesis of nanophase particles has been carried out most frequently by physical methods based on evaporation-condensation (gascondensation), high pressure sputtering, laser ablation and plasma processing [1, 4]. The main drawbacks to these processes include low production rates and difficulties encountered in producing multicomponent materials. In addition, methods such as evaporation/condensation are applicable only to materials having sufficiently high vapor pressures at moderate temperatures. Thus, there is a considerable need to develop processing techniques to produce nanophase materials in bulk quantities in a controlled and highly reproducible manner.

Spray pyrolysis or aerosol decomposition is capable of producing high-purity, unagglomerated, submicron size powders with either homogeneous chemical composition or controlled phase distribution (composite materials) [5, 6]. Recently, Carim et al. [6] and Lyons et al. [7] have demonstrated the application of spray pyrolysis to the generation of nanophase single- and multi-component metal oxide powders. This approach involves droplet generation, solvent evaporation, precursor precipitation, and decomposition of precursors within the particles. The grain size is kept small by operating at temperatures which are sufficient for the complete decomposition of the precursors, but not high enough to cause excessive grain growth.

In this work, we have examined the generation of fine-grained superconducting ceramic particles ((Bi, Pb)-Sr-Ca-Cu-O). The motivation to produce ultrafine-grained particles of (Bi, Pb)-Sr-Ca-Cu-O system of superconductors came from the fact that the formation of the desirable (Bi, Pb)₂Sr₂Ca₂Cu₃O₁₀ phase (T_c = 110 K) via conventional solid-state reaction route needs prolonged high temperature processing (~15 days). Aerosol decomposition can produce powders having the required intermediate phases homogeneously mixed at the nanophase level which would enhance the subsequent formation of the desired high temperature superconducting phase during powder processing.

We have also examined aerosol processing of fullerenes. Fullerenes (C_{60} , C_{70} , etc.), the recently discovered family of allotropes of carbon, and related materials have a variety of interesting properties such as superconductivity, ferromagnetism, and non-linear optical behavior, and are important from both fundamental and technological viewpoints [8, 9]. They are soluble in hydrocarbon solvents and have appreciable vapor pressures above 500 °C [8, 10], and hence are perfect candidate materials to employ several liquid (spray)- and vapor-phase aerosol routes to generate nanophase fullerene-based materials.

Currently, we are developing spray and gas-to-particle conversion routes to obtain a variety of nanophase materials including ceramic superconductors and single metal oxides, and metal-fullerene composites and compounds. In this paper, we report the results obtained during



Fig. 1. Apparatus for spray drying and spray pyrolysis.



Fig. 2. Microstructure evolution during spray pyrolysis.

the generation of nanophase particles of these materials with an emphasis on pure fullerenes and their nanocomposites with metals.

EXPERIMENTAL

Spray drying and pyrolysis were applied for the generation of nanophase particles of pure fullerenes and their composites with rhodium, and (Bi, Pb)-Sr-Ca-Cu-O and its composites with silver metal. The experimental system has been described previously [11] and is shown schematically in Fig. 1. In brief, the aerosol flow system consisted of a mullite or quartz tube (3.25 in. I. D., 36 in. heated length) in a three-zone furnace (Lindberg). Droplet generation was carried out by TSI-3076 or BGI Collison aerosol generators using compressed nitrogen or air (35 psi) as a carrier gas. The powders were collected onto nylon filters which were heated to 48-65 °C to prevent condensation of the solvents.

Nanophase fullerene particles were generated by spray drying a solution of pure C₆₀ or mixed fullerene extract (MFE, 85-15% C₆₀/C₇₀) (Texas Fullerene Corp.) in toluene using nitrogen as a carrier gas [12]. Spray drying was carried out at 150 to 200 °C so that solvent removal was complete without excessive grain growth within the particles. Nanocomposites of fullerenes with rhodium were obtained by spray pyrolysis of solutions of MFE and [(1,5-COD)RhCl]₂ in toluene at 550 °C. Although [(1,5-COD)RhCl]₂ (where COD= cyclooctadiene) decomposes to Rh metal at 335 °C under nitrogen [13], a reactor temperature of 550 °C was necessary to achieve complete decomposition of the rhodium precursor within a reactor residence time of 15 s. Ultrafine-grained particles of (Bi, Pb)-Sr-Ca-Cu-O and their composites with silver were produced by aerosol decomposition of a stoichiometric mixture of nitrate solutions (0.05 M with respect to Sr²⁺) at 700 to 900 °C using air as a carrier gas.

Nanometer-size (30-40 nm) particles of fullerenes (C_{60} , C_{70} , etc.) were also generated by vapor condensation starting from pure C_{60} or MFE using nitrogen carrier gas [14]. Batches of 100 mg of pure C_{60} or MFE were loaded at the center of the tube and heated to 400-650 °C at a rate of 2 to 4 °C/min. While heating, the temperature was held at 250 °C for one hour to remove any solvent remaining in the powders. Particles formed were collected in-situ onto polycarbonate filters and copper grids for scanning and transmission electron microscopy.

The powders produced were characterized by a variety of techniques. Total particle concentrations were monitored with a condensation particle counter (CPC, TSI Model 3022). Number size distributions in the size range 0.02-0.7 μ m were monitored with a differential mobility analyzer (DMA, TSI Model 3071). The DMA data were corrected for diffusional losses and inverted using the TSI inversion routine. X-ray diffraction (XRD) (Cu K α) was used to identify the crystalline phases in the powders, providing information about phase purity and



- Fig. 3. Bright-field TEM micrograph of nanophase fullerene particles made by spray drying at 200 °C under nitrogen.
- Fig. 4. TEM micrograph of 50/50 wt.% MFE/Rh nanocomposite powders made at 550 °C under nitrogen (insert is a selected area diffraction pattern).

extent of reaction. Scanning electron microscopy (SEM) (Hitachi Model S-800) was used to study the morphologies of the particles. Transmission electron microscopy (TEM) (JEOL 2000 FX, 200 kV) was used to investigate the microstructure and crystallanity of the powders. Bright- and dark-field TEM images and X-ray diffraction peak broadening were used to estimate the grain or crystallite sizes in the powders.

RESULTS AND DISCUSSION

The process of forming nanocrystalline powders by aerosol decomposition consists of drying micron-sized droplets accompanied by precursor precipitation and is followed by intraparticle reactions as the particles flow through the hot-wall reactor. Grain-size can be kept small by operating at temperatures which are sufficient for the complete removal of the solvent and decomposition of precursors, but not high enough to cause excessive grain growth within the particles (Fig. 2). In the case of pure fullerene particles, the process was simply spray drying with the dried, ultrafine fullerene particles having a small grain size. Figure 3 is a brightfield TEM micrograph of pure, solid, polycrystalline fullerene particles having 30-40 nm size made in nitrogen at 200 °C. The particles had several regions showing lattice fringes with a spacing of about 8.2 Å which corresponds to the prominent (002) d-spacing of C₆₀. The corresponding X-ray diffraction pattern showed extensive peak broadening corresponding to a grain-size of about 10 nm. A TEM micrograph of MFE/Rh = 50/50 wt% powders (Fig. 4) showed 20 to 50 nm size particles having dark rhodium grains dispersed in the fullerene matrix. The rhodium particles had a crystallite size of 3-5 nm consistent with the crystallite size observed by XRD peak broadening. The selective area diffraction pattern (Fig. 4) showed rings corresponding to the prominent d-spacings of C60 and Rh. In this study, rhodium was chosen just to demonstrate the application of spray pyrolysis to fullerene-metal systems. This approach can easily be extended to other metals which may form nanocomposites or compounds with fullerenes.

In previous work, aerosol decomposition was useful in producing submicron particles having a nominal composition of Bi_{1.8}Pb_{0.44}Sr₂Ca_{2.2}Cu₃O₁₀ consisting of a mixture of phases having a grain size of 20-60 nm [11]. These powders could subsequently be converted to the corresponding high-temperature superconducting phase by sintering in air at 850 °C for just 16 h [11]. Similarly, the formation of the YBa₂Cu₄O₈ compound was achieved at ambient pressure using aerosol-synthesized powders compared to high pressure synthesis required in the conventinal solid-state route [15]. Here we present the extension of this approach to the Ag-Bi-Pb-Sr-Ca-Cu-O system. Figure 5 shows a TEM micrograph of as-synthesized composite powders of 10 wt.% Ag-90 wt.% Bi_{1.8}Pb_{0.44}Sr₂Ca_{2.2}Cu₃O₁₀. The particles were







Fig. 6. Gas-phase number size distributions of particles formed during the generation of Bi_{1.8}Pb_{0.44}Sr₂Ca_{2.2}Cu₃O₁₀ by spray pyrolysis at different temperatures

polycrystalline with a grain size of 20-60 nm. One advantage of this route is the ability to obtain a fine dispersion of silver in the composite powders. The gas-phase particle size distributions for different processing temperatures were determined using a differential mobility analyzer. Figure 6 shows the number size distribution at the temperatures of 200, 500, 700, 800 and 900 °C. The average particle diameter of 0.13-0.14 μ m for dried nitrate particles at 200 °C reduced to 0.09 and 0.08 μ m at 700 and 800 °C, respectively, due to intraparticle reactions and densification. An important aspect of studying gas-phase particle size distribution in this system was understanding the lead-loss as a function of particle size during powder synthesis. Earlier, from bulk chemical analysis, 10, 40 and > 80 % of the initial lead was lost during powder synthesis at 700, 800 and 900 °C, respectively [11]. Lead oxide evaporated from the particles reacted with the walls of the reactor tube or condensed onto the colder ends of the tube. In this work we have shown that new particles having an average diameter of 0.015-0.03 μ m were formed from lead oxide vapor at 900 °C. This demonstrates the overlap between spray pyrolysis and gas-to-particle conversion approaches.

Figure 7 is a SEM micrograph of fullerene nano-particles formed via vapor condensation at 500 °C. The particles were solid, unagglomerated and spherical in shape for the range of temperatures studied (400-650 °C). Transmission electron microscopy indicated that the particles were partly amorphous at 400 °C and became crystalline C60 for processing temperatures of 500 °C and above. Fullerenes, due to their high vapor pressures above 500 °C [10], vaporized at the reactor temperatures used (400-650 °C) and the vapors were carried through the reactor by nitrogen carrier gas. The mixture of fullerene vapors and nitrogen cooled beyond the hot-zone of the reactor, thereby increasing the saturation ratio which led to the formation of ultra-fine fullerene particles via homogeneous nucleation, condensation and coagulation. The physico-chemical phenomena occurring during fullerene particle formation via vapor condensation is schematically shown in Fig. 8. Figure 9 shows the number size distributions in the gas-phase at the processing temperatures of 500, 525 and 550 °C during vapor condensation of fullerenes. The particles had an average size of 30, 35 and 40 nm, and a total number concentration of 2.2x106, 3.5x106 and 5.0x106 #/cm3 at 500, 525 and 550 °C, respectively. Thus, from the SEM, TEM and DMA results, we have demonstrated the application of vapor condensation to generate nanophase (30-40 nm), solid, spherical and unagglomerated fullerene particles.

ACKNOWLEDGEMENTS

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Fig. 7. SEM micrograph of fullerene nano-particles formed via vapor condensation at 500 °C.







Fig. 9. Number size distributions in the gas-phase at the processing temperatures of 500, 525 and 550 °C during vapor condensation of fullerenes.

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SnO₂ production by an electrostatic spray pyrolysis process.

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Abstract

In this work a powder of SnO_2 has been produced by electrostatic spraying of a precursor solution of $Sn(Ac)_4$ in absolute ethanol and subsequent drying and pyrolysis of the produced liquid droplets. The advantage of the electrostatic spraying is the small size of the produced primary droplets and the narrow size distribution of these droplets. After the optimal spraying conditions had been found a number of experiments have been done to determine the influence of the concentration of the precursor solution, the oven temperature and the residence time in the oven.

The main conclusion that can be drawn from this work is that the concentration of the precursor solution is the most important factor influencing the particle size and shape.

Keywords

SnO₂; Taylor cone; Aerosol Reactor;

Introduction

For the production of high quality ceramic components, very pure, submicron particles, with a narrow size distribution are required. Aerosol processes for the production of these materials are very attractive, since they enable the production of very small and extremely pure particles. High tonnages of commodity materials, as TiO_2 are manufactured via the gas to particle route and recent research indicates good potential for the synthesis of high temperature structural ceramics as Si_3N_4 in this way.

Much more complex compounds can be made via the other aerosol route, viz. the atomization of a solution into droplets and the consequent drying/pyrolysis/reaction to form solid particles. Commercially MgO is manufactured in that way and in the laboratory different multicomponent ceramic powders, such as superconducting $Y_1Ba_2Cu_3O_7$ can be obtained. However conventional atomization techniques are not suitable for this process, as they produce relatively large droplets with a broad size distribution.

In this work an electrospray is used. This spraying technique uses the so called Taylor cone which produces *primary* droplets in the order of 1 μ m. In this way it is possible to produce submicron powders. At the Delft University of Technology an aerosol generator based on this principle has been developed some years ago [1]. A generator as described in a more recent paper has been used [2].

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The aim of the research is to produce a submicron powder of SnO_2 . Different precursors can be used, e.g. $SnCl_4$, $SnOCl_2$ or $Sn(Ac)_4$. Of these compounds the latter was chosen because pyrolysis of the chloride containing compounds leads to Cl_2 or HCl, neither of which are desirable. SnO_2 is a semiconductor material that is used in the electronic industry or as an additive to alter the electric properties of powders.

The Delft Aerosol Generator (DAG)

In a strong non-uniform electric field ($\approx 10^6$ V/m), a pendant drop will deform into a conically shaped volume of liquid. In a well known paper published by Taylor [3] the conditions were studied under which this conically shaped surface, under the influence of an electric field, could exist. From the tip of the Taylor cone (fig. 1) very small droplets (≈ 1 μ m) are ejected.



Figure 1. The Taylor cone

This principle can be used as the basis for an aerosolgenerator. A schematic diagram of the aerosol generator is shown in figure 2. The liquid is fed to a nozzle whose inner diameter can vary in our set up from 0.1 to 1 mm. This relatively large opening ensures that there are no problems with small particles clogging the nozzle, whilst the droplets produced are two to three decades smaller than the nozzle opening. The outside diameter can vary from 0.1 to 1 cm. The nozzle is constructed from a conducting metal. Constant flow is maintained by using a syringe pump. This pump gives a flowrate from 0 to 99.9 ml/h with an accuracy of 0.1 ml/h. Usual flowrates are in the order of 10 ml/h

The aerosol generator itself consists of three functional parts; namely, the nozzle and spraying system, the metal needle acting as the discharger and a metal ring which has the function of a shielding electrode. The nozzle is connected to a positive high voltage source variable in the range of 0-18 kV DC. With the nozzle to ring distance equal to 2-3 cm, a voltage difference of 5-10 kV is usually enough to create a stable cone for semiconducting liquids.



Figure 2. Schematic drawing of the Delft Aerosol Generator

The discharging electrode consists of a metal needle which is earthed. The third component, the shielding ring, is maintained at the same polarity as the nozzle. The electric field created between the ring and the needle has to be strong enough to create a corona discharge at the tip of the needle, supplying negative ions to neutralize the generated, highly charged droplets. The shielding ring is essential for the satisfactory operation of the generator. Without it the liquid cone is very unstable. So the shielding ring with a voltage, usually in the range of 4-8 kV DC has two functions. It creates a strong electric field causing a corona discharge at the needle and also stabilizes the field between nozzle and ring giving a stable liquid cone and a more concentrated stream of droplets.

Experimental Section

Preparation of the precursor solutions

The precursor material is a coarse powder of $Sn(Ac)_4$, with a small (but unknown) percentage of impurities. This powder was dissolved in absolute ethanol. The solution was stirred for two hours and filtered to get rid of the impurities. A number of different solutions have been prepared (table 1).

Solution	1	2	3	4	5	6	7
Sn(Ac) ₄ in g	0.813	2.255	3.232	3.886	5.064	8.070	4.050
V in ml	200	200	200	205	200	204	100
C1 in %(w/w)	0.5	1.4	2.05	2.4	3.2	5.0	5.1

lable	1.	Molar	and	weight%	concentration	of	the	solutions

The contact of water with these solutions instantaneously creates a grey gel which also appears after some time when the solutions are just in contact with air. To avoid the formation of the gel during the preparation of the solutions all the glassware was dried in an oven at 100 °C and absolute ethanol (analytical pure) was used because 100% pure ethanol (which is obtained by distillation) still contains traces of water and thus leads to the gel. The concentration of the solution plays a big role in the gelatinizing process. For example a pendular droplet of the 5% solution will become a gel after 30 seconds when the pump is switched off whereas for the 0.5% solution the gel will become visible after about 3-4 minutes.

It is thought that the observed gelification is the result of the polymerisation of Sn atoms. Nevertheless the acetate must play an important role in the polymerisation proces because the polymers of tin are not stable at high temperatures, whereas this gel is.

Generator-Reactor design

For this research a reactor has been designed as shown schematically in fig 3. It has been designed according to two criteria:

- The DAG should be included in the reactor to produce the aerosol directly in it. This
 presents two advantages. The produced aerosol can easily be guided into the oven and
 the temperature of the air in the vessel is controllable.
- The shape of the reactor should be such as to assure no turbulence in it because turbulence increases the deposition of particles on the wall and agglomeration.



Figure 3. Schematic drawing of the "reactor"

The reactor is made of pyrex and can stand temperatures upto 600 °C. With flow visualisation (using cigarette smoke), the flow in the reactor has been studied.

The disadvantage of this reactor is the long residence time the particles have before they enter the tube oven. Therefore a number of experiments has also been carried out without this reactor.

Two different tube ovens have been used. One was 62 cm long with an inner diameter of 3.2 cm. It has a temperature range from 20 °C to 600 °C with an accuracy of \pm 5 °C. At a distance of 4 cm from the in- and outlet, the temperature is already the one indicated by the oven, as was measured with thermocouples.

The other was 32 cm long with an inner diameter of 2.5 cm. It has a temperature range from 20°C to 1200°C with a high accuracy (± 2 °C). At a distance lower than 2 cm from the entrance the temperature (controlled by thermocouples) is already the one indicated.

The tubes, used in these ovens, were 80 cm long with an inner diameter of 2.7 cm, and 50 cm long with an inner diameter of 2.2 cm. Both of them were of quartz and can stand temperatures upto 1100°C.

Production of SnO₂

Some initial experiments have been done to obtain the best values for the potential differences between nozzle-ring and ring-needle. From earlier work [4] it is known that these potential differences have little or no influence on the particle sizes after spraying. Therefore it was decided to keep the values, for which the Taylor cone seemed to be the most stable, constant. All further experiments were done with voltage differences of the order of 8 kV between nozzle and ring. The same is true for the voltage difference between ring and needle and this was kept constant at ≈ 6 kV and a distance of 6.5 cm between ring and needle point.

After these initial experiments an experimental study has been performed to investigate the influence of the following variables: residence time in the oven, temperature in the oven, concentration of the precursor solutions and temperature in the spraying section.

The particles were collected on a filter and analyzed by electronmicroscope (SEM). The powder production rate is very low (0.166 g/h for a liquid flowrate of 10 ml/h and a precursor concentration of 5 %(w/w), assuming a collection efficiency of 100%). So it takes about 0.5 hour to obtain a reasonable amount for analysis.

Results and Discussion

Experiments with the designed reactor

The experimental set up is shown schematically in figure 4a. The conditions used in these experiments are listed in table 2.

Experiments 1-4 were done with the reactor and two ovens. One before and one after the reactor (fig. 4a). The shape of the particles obtained under those conditions is quite indescribable. A SEM picture of those particles can be seen in figure 5.

Experiments number 6,7 and 8 have been realised without heating the blowing air. When the temperature of the oven is 500 °C or 600 °C the particles obtained have two shapes: either they look like a cup (or a bowl) or like spheres. The cup shaped particles are quite big (between 1.5 and 2.5 μ m) compared to the spherical particles which are mostly submicron sized. When the same experiment is done with an oven temperature of 250 °C (exp. 8), the particles obtained are only cup shaped, and they are bigger (around 3 μ m of average diameter). See figure 6.

Exp. #	Solution %(w/w)	Residence time in the oven (s)	Temperature in the oven (°C)	Temperature before the reactor (°C)	ΔV (nozzle- ring) (kV)	Flowrate solution (ml/h)
1	2.05	0.5	815	250	7.6	9
2	2.05	0.5	815	450	7.6	9
3	2.05	0.5	1008	450	7	10
4	2.05	0.5	1008	600	7	10
5	2.05	no oven	no oven	550	7.6	8
6	3.2	1.55	600		8.2	8
7	3.2	1.6	500	radial and for	8.8	8
8	3.2	1.65	250	antitic club writer of	7.6	8

Table 2. Experimental conditions for the experiments with the reactor



Figure 4. Experimental setup: A) with reactor and B) without reactor

a) High Voltage cablesb) Flowmeter

e) Valve

f) Insulator block with nozzle

- c) Pump
- d) Syringe pump
- g) Shielding ring
- i) Tube ovenj) Air inletk) Taylor cone
- h) Discharging needle





Figure 5. SEM picture of the particles obtained by the high temperature experiments

Figure 6. SEM picture of the cup-shaped particles

Experiment 5 has been carried out without an oven behind the reactor but the air entering the reactor was heated at 550 °C. The filter was placed just behind the reactor and some powder was collected and analysed. In this case the obtained particles also display two shapes. Either they are spheres (between 0.5 and 1.5 μ m) or donuts (between 1.5 and 3.5 μ m).

Experiments without the designed reactor

These experiments can be divided in two parts, short and long residence times.

Short residence times (0.5-8 sec.)

The conditions used in these experiments are summarized in figure 7. The experimental set up is shown in figure 4b.

The parameters tested are the concentration of the precursor solutions, the temperature in the oven and the residence time in the oven. In the following table the precise values of the conditions are given for some of the experiments which will be discussed in the text.



Figure 7. Schematic "map" of the experiments done

Table 3.	Experimental	conditions	for	the	low	residence	time	experiments	without	the
	reactor									

Exp. #	Solution %(w/w)	Residence time in the oven (s)	Temperature in the oven (°C)	ΔV (nozzle- ring) (kV)	Flowrate solution (ml/h)
9	2.36	1.25	400	10	6
10	5	1.2	400	8.2	9
11	0.5	1.2	400	8.2	9
12	0.5	1	200	8.2	8
13	0.5	1.2	608	8.2	9
14	0.5	1.2	815	8.2	9
15	0.5	1.2	1008	8.2	9
16	0.5	3.8	1008	8.2	9
17	5.1	3.8	815	8.2	6
18	5.1	3.8	1008	8.2	6

The influence of the concentration of the precursor solution on the produced powder can be deduced from experiments 9, 10 and 11. For these three experiments size distributions of the powders have been made by hand from the SEM-pictures. Although it is a very rough method it gives a good indication. For the experiments 10 and 11 the result is given in figure 8.



Figure 8. Particle size distributions, obtained from SEM pictures

It is clear (and not only from these two figures) that the distribution broadens with increasing concentration. The number average diameter is 1.61 μ m, 2.09 μ m and 1.87 μ m for the concentrations 0.5%, 2.4% and 5% respectively. From these results it is difficult to deduce the influence of precursor concentration on the diameter. The shape of the particles produced in these three experiments is more and more spherical with decreasing concentration, while at the same time the surface of the particles gets smoother.

The effect of the temperature can be studied with the experiments 11-15. The concentration is 0.5% and the residence time is 1.2 s. The temperatures are 200, 400, 608, 815 and 1008 °C. The relation between the temperature and the average diameter of the produced particles is not obvious. Only at 1008 °C the spherical particles are bigger than in the other experiments while at the same time the number of fragments increases with increasing temperature.

Experiment 15 shows a narrowing of the size distribution with increasing residence time. On the SEM picture of this experiment a lot of fragmented particles can be seen.

The results of experiments 17 and 18, where high concentrations and high temperatures are used, are very interesting. The particles produced in these two experiments are rather large ($\approx 3-8 \ \mu m$) and the number of submicron particles is very low.

The interpretation for short residence times of the formation of the different shaped particles in these experiments can be done in a similar way as described by Charlesworth et al. for spray drying [5]. A droplet starts to evaporate and after some time a solid crust is formed. This solid crust is subjected to an inflation due to the evaporation of the remaining liquid inside the hollow particles. This research proves that the properties of the solid crust which is formed during the spray drying process highly depends on the concentration of the precursor solution. When this concentration is low (0.5%) the solid crust formed is smooth and flexible. It easily explodes, under high temperatures and thus prevents the formation of big (>3 μ m) hollow particles. But the fact that the inflation phenomenon takes place leads to the formation of particles larger than 1 μ m in diameter.

When the concentration is high, the solid crust which is formed is stronger. And that permits the inflation phenomenon to take place during a longer time and thus leads to bigger particles.

To produce more fragments some experiments were done with higher residence times and high temperatures.

Long residence times (60-240 sec.)

A number of experiments have been done with residence times between 1 and 4 minutes. This was done by trapping the air in the oven for a certain time and taking a sample with a thermophoretic sampler. It was observed that the number of small particles (in the order of 100-200 nm) increased a lot. Unfortunately it was impossible to obtain sharp SEM pictures of these particles. But also big particles were found in these experiments (although the number was much smaller than in the other experiments). These big particles were hollow and some of them were partly exploded or shrivelled, see figure 9. Therefore it is concluded that the small particles found in these experiments were formed by explosions of bigger particles.



Figure 9. SEM pictures of particles found in the long residence time experiments

Conclusions and Future Work

It has been proven in this work that electrostatic spraying can be used for the production of SnO_2 powder from $Sn(Ac)_4$. It is possible to operate the Taylor cone stably for at least 8 hours. The advantage of this method is that the particles obtained are smaller than in conventional spraying methods. A disadvantage is the very low production rate (mg/h). This is valid for 1 Taylor cone and the scale up has to be done by a multiplication of the number of Taylor cones, which is not very difficult in principle. The sizes of the particles produced by this electrostatic spraying method is usually in the order of 1 μ m. Therefore it was thought that by using solutions it should be no problem to generate submicron particles. This research has proven that it is in fact not so easy (at least for the material under consideration) to do so. The reason for this is that the drying of these micronsized particles is not easy and not well understood. Depending on the process conditions one can obtain fragmented particles (well below 1 μ m in size), cup-shaped particles and hollow and/or porous spheres (varying in size from 1-8 μ m). The most important variable influencing the shape of the produced with high temperatures and low concentrations.

For industry it is not very interesting to work with these low concentrations, especially when the solvent is something like 100% pure ethanol.

Future work starts with a study of the drying process. More experiments will be done and furthermore the authors are working on a model to describe the drying of droplets containing dissolved solids. The authors believe that this is the key to succesfully develop spray pyrolysis processes like the one described in this paper. Secondly, the reactor used in this work needs some redesigning because it is very inconvenient to work in the open air. Finally, for practical reasons, the process will be scaled up.

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Titania Powders by Hydrolysis and Oxidation of TiCl4

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ABSTRACT

The competition between hydrolysis and oxidation of TiCl₄ during vapor phase synthesis of titania powders was experimentally investigated. The effects of reactor temperature, reactant mixing and H₂O/TiCl₄ ratio were studied in a hot wall aerosol flow reactor. The presence of water vapor resulted in rounded particles instead of the faceted ones observed in the absence of water; this effect was most pronounced at lower reactor temperatures. Mixing the water and TiCl₄ vapor streams at low temperature resulted anatase titania while at high temperatures resulted mostly rutile. Larger aggregates with smaller primary particles were observed for powders synthesized in the presence of water vapor. The mixing temperature of the water and TiCl₄ vapors as well as the H₂O/TiCl₄ ratios did not affect the aggregate size or specific surface area.

INTRODUCTION

The competition between oxidation and hydrolysis of precursor vapors is commonly encountered in flame synthesis of fumed silica and titania. Though these are mature technologies, a fundamental understanding of the role of these chemical routes in determining particle characteristics is still lacking.

In the manufacture of optical fibers, Bautista and Atkins (1991) examined the competition between oxidation and hydrolysis of silicon tetrachloride (SiCl₄) in a diffusion flame. During pure oxidation, nearly 100% particle deposition efficiency was obtained while the deposition efficiency was lower during concurrent oxidation and hydrolysis of SiCl₄. The crystallinity of flame synthesized powders is also affected by the presence of water. In the synthesis of oxide powders in hydrocarbon assisted flames, water is present from hydrocarbon combustion. Frequently, aqueous solutions of additives are sprayed into the flame to control particle morphology and size. The oxidation and hydrolysis of TiCl₄ is chosen as a model system because of the commercial importance of titania and the innovative applications that have recently been proposed for it. In these applications the particle morphology, degree of aggregation, size distribution or phase composition are key powder characteristics which must be controlled.

Flames are complex systems. In order to deconvolute the effects of water from other chemical effects, experiments were conducted in a hot wall reactor. This reactor allows operation with controlled temperature and residence time where stoichiometry and the mixing point of the reactant and aqueous streams are well defined. The effect of Si, P, Al and other additives on titania particle characteristics has been studied extensively (Mezey, 1966; Suyama and Kato, 1985; Akhtar et al., 1992). The purpose of this paper is to investigate experimentally the effect of water on the morphology, size, degree of aggregation and phase composition of titania powders synthesized by gas phase oxidation and hydrolysis of TiCl₄.

EXPERIMENTAL

Titania particles were synthesized at a reactor residence time of about 1.2 s (at 1473 K) and at furnace set temperatures of 1273, 1473 and 1673 K,. The precursor TiCl₄ vapor was introduced into the reactor at a constant rate of 1.4×10^{-4} mol/min during all experiments and the molar H₂O/TiCl₄ ratio ranged between 0.03 and 5. The schematic of the experimental apparatus is shown in Figure 1 of Akhtar et al. (1992). All experimental and powder characterization procedures are identical to those employed here with only exception the water feed to the reactor.

Water droplets generated in nitrogen by a modified home humidifier (Ultra-Mister, Tatung) are carried into the reactor with a ceramic tube which is concentric with the TiCl₄ feed tube (Figure 1). The point of mixing of TiCl₄ and water vapors is controlled by moving this tube along the reactor axis at various distances (a= -4cm, b= 0 cm, c= 5 cm, d= 8 cm, and e= 13 cm) from the start (point b) of the furnace. The reactor tube section inside the furnace is 60 cm. The temperature along the reactor axis increases approximately linearly till it reaches the set temperature about at 14 cm inside the furnace (Akhtar et al., 1991). The table in Figure 1 shows the mixing point temperatures for the three furnace set temperatures used in this study.

The amount of water vapor introduced into the reactor was measured by using an aqueous NaCl solution (0.05 g/ml) in the humidifier. Salt particles were collected on filters downstream of the reactor at a constant nitrogen flow rate. From the concentration of the solution in the humidifier and the weight of NaCl collected on the filter, the amount of water vapor introduced into the reactor was determined (Akhtar, 1993).

RESULTS AND DISCUSSION

Titania exists in three polymorphic forms - rutile, anatase and brookite. Rutile is the thermodynamically stable form while anatase and brookite are metastable at all temperatures and transform to rutile on heating (Rao et al., 1961). Under the process



Mixing Point	Position from start of	Furnace Set Temperature =	Furnace Set Temperature =	Furnace Set Temperature =
김 김 것 한 문	Furnace (cm)	1273 K	1473 K	1673 K
a	- 4	498	529	542
b	0	599	670	694
с	5	811	986	1026
d	8	941	1132	1230
е	13	1273	1473	1673

Figure 1: Reactor schematic with the different mixing points and the respective temperatures.

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conditions employed in this work, the titania powders are primarily anatase with some rutile present (Akhtar et al., 1991). Anatase has a more open structure and is the phase initially formed. The thermodynamically stable rutile phase has a higher energy of formation and cooperative movement of the Ti⁴⁺ and O²⁻ ions is needed for the formation of the more compact rutile crystal (Shannon and Pask, 1964).

The effect of process temperature on the rutile content of titania powders made at a H₂O/TiCl₄ ratio of 0.06 and the TiCl₄ and water vapors mixing at various points is shown in Figure 2. The intensity of the primary rutile reflection (110) increases with increasing temperature showing that the weight % of rutile increases with temperature: from 0 at 1273 K to about 16% at 1673 K. The increase in rutile content with increasing temperature is consistent with the observations for pure titania (Akhtar et al., 1991) and with the anatase to rutile phase transformation mechanism proposed by Shannon and Pask (1964). At higher temperatures, the cooperative movement of Ti⁴⁺ and O²⁻ ions involves the rupture of two of the six Ti-O bonds to form new bonds. The rate of bond break-up is enhanced at the higher temperatures resulting in faster transformation to the rutile phase.

Figure 2 also shows that at the set temperature of 1273 K, all the product crystalline powder is anatase and the mixing point has little effect on the phase composition. At higher furnace set temperatures, the rutile content increases as the mixing of the TiCl₄ and water vapors takes place further inside the furnace into the high temperature zone. Mixing the vapors 4 cm outside the furnace where the temperature is low (542 K for a furnace set temperature of 1673 K) makes TiCl₄ hydrolysis the dominant conversion route resulting in hydrous titania. On passing through the reactor at high temperature, these powders lose water and crystallize to the anatase form. If the residence time and temperature are sufficiently high then some of the powders are further transformed into rutile. As the mixing point of TiCl₄ and water vapors is progressively moved further into the furnace, the mixing temperature increases (1673 K at 13 cm inside the furnace for a set temperature of 1673 K) and more TiCl₄ is oxidized than is hydrolyzed. The powders formed when TiCl₄ and water mix at the highest temperatures contain the highest rutile fraction in agreement with Oguri et al. (1988) and Hebrard et al. (1990).

For mixing of the water and TiCl₄ streams 4 cm outside the furnace ("a" in Figure 2), almost all of the powder is probably formed by hydrolysis and is primarily anatase. For reactant mixing further downstream, the role of oxidation becomes dominant and at a mixing point 13 cm from the start of the furnace ("e" in Figure 2) 16% rutile is observed in the powder. The latter value is in agreement with the amount of rutile observed in titania powders made in the absence of water (Akhtar et al., 1991). This confirms that high furnace set temperatures and mixing of TiCl₄ and water vapor



Figure 2: Rutile content of titania powders made at three furnace set temperatures for different mixing points of H2O & TiCl4 vapors and H2O/TiCl4 ratio of 0.26



Figure 3: Aggregate titania particle size distributions made at 1473 K, TiCl4-water vapor mixing at the start of the furnace and different H2O/TiCl4 ratios

streams in the high temperature region reduce the impact of hydrolysis on titania phase composition.

As the H₂O/TiCl₄ ratio in the reacting stream was increased, the rutile content decreased. At the higher H₂O/TiCl₄ ratio, more TiCl₄ is hydrolyzed than is oxidized resulting in lower rutile content. This again illustrates that the hydrolysis product is mostly anatase. These results also are in agreement with the thermodynamic analysis that indicated that hydrolysis becomes more significant with increasing H₂O/TiCl₄ ratio in the reacting stream (Akhtar 1993).

Figure 3 shows aggregate particle size distributions for titania made at 1473 K furnace set temperature and different $H_2O/TiCl_4$ ratios. The presence of water vapor leads to a slight increase in aggregate size but varying the $H_2O/TiCl_4$ ratio in the process stream has little effect on the aggregate size determined from the DMPS. The same behavior is observed for powders made at 1273 K, an increase in aggregate size with the introduction of water vapor and no further effect with further increasing $H_2O/TiCl_4$ ratios. Changing the mixing point too has little effect on the aggregate size increased with the presence of water, the spread of the distribution remained essentially unchanged between 1.5 and 1.6 (Akhtar, 1993). The aggregate size for titania made at 1673 K is quite insensitive to the presence of water and to the temperature at the mixing point.

In all cases, the aggregate size decreased slightly with increasing temperature. The flow rate of the gases was kept constant in all the experiments. With increasing expansion of the gases at higher temperatures, the residence time in the reactor was shorter. Titania particles grow by coagulation. Decreasing residence time leads to a decrease in the time for collision and results in smaller aggregates. For particle growth by coagulation in the free-molecular regime, the diameter of particles increases with residence time as t^{1/3} while with temperature dependence as T^{1/6}. On maintaining constant reactor residence time, Akhtar et al. (1991) found that titania aggregate size increased with temperature due to increased collision frequency among aggregates at higher temperatures.

The average aggregate size obtained from the differential mobility paticle sizer (DMPS) was in reasonable agreement with the maximum extent size of the compact aggregates observed under the TEM (Akhtar 1993). For particles made at 1473 K, mixing TiCl₄ and water vapor 8 cm inside the furnace (at "d" in Figure 2), and at $H_2O/TiCl_4$ ratio of 0.06, the average diameter obtained from the DMPS was 0.23 µm while that measured from TEM micrographs was 0.32 µm. Besides compact aggregates, some long chain-like aggregates were also observed on the micrographs and the average size of the latter was about 0.6 µm. The DMPS measures an

average mobility equivalent diameter which will be closer to the equivalent spherical diameter but smaller than the maximum extent diameter observed on micrographs.

The location of the mixing point of TiCl₄ and water vapor streams did not affect the specific surface area of the product titania. This was consistent with microscopic observations (Akhtar, 1993). The average primary particle diameter determined from BET analysis was 0.05 μ m for titania made at 1473 K at a H₂O/TiCl₄ ratio of 0.06 and mixing TiCl₄ and water vapor at the start of the furnace while the diameter from TEM was 0.03 μ m. For powders made at the same conditions but mixing TiCl₄ and water vapor 8 cm from the start of the furnace (at "d") the primary particle diameter from BET surface area measurements was 0.05 μ m and that obtained from micrographs was 0.04 μ m. In general, the specific surface area of titania decreases with temperature at all mixing points since particles sinter faster at high temperatures.

At all set and mixing temperatures the specific surface area increased with the introduction of water vapor but further increasing the $H_2O/TiCl_4$ ratio had little effect. Crystallite sizes (obtained from X-ray line broadening) of titania made in the absence of water are larger than those of titania made in the presence of water at constant furnace set temperatures. Changes in $H_2O/TiCl_4$ ratio have no significant effect on crystallite size. These results are in agreement with specific surface area measurements (Akhtar, 1993).

Readey and Readey (1987) reported significant increase in the grain size of titania sintered in the presence of water vapor though the densification rates were not affected for experiments conducted at 1573 K for 5 hours. Quantitative modeling shows that the rate limiting steps involved in faster sintering and surface area reduction of titania in the presence of water are the formation of volatile Ti(OH)₂Cl₂ and the diffusion of hydroxyl ions (Gruy and Pijolat, 1992). These findings would seem to contradict the present results of high surface area titania being formed on the introduction of water vapor. However, it should be borne in mind that in the experiments reported here, the presence of water vapor presents an alternative route for TiCl₄ conversion: hydrolysis. Titania formed by hydrolysis has a higher specific surface area than that formed by oxidation (Clark, 1975). It is the presence of titania made by the hydrolysis route that leads to the increase in specific surface area observed experimentally. If these powders had been further exposed to the 3-5 hours residence times as reported in literature then they too would have sintered further and reduced their specific surface area.

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Particle Formation in a Laser-heated Aerosol Reactor with Application to Silicon and Silicon Nitride Synthesis

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Keywords

Laser-Chemical Vapor Precipitation; Silicon; Silicon Nitride; CVD Phase Diagrams; Homogeneous Nucleation; Aggregation; Sintering; Controlled Gas Mixing; Image Analysis; Thermophoretic Sampling System.

Introduction

Highly homogeneous and stable industrial materials which do not occur naturally are produced commercially by use of artificially synthesized starting materials, inorganic nonmetallic solids with ionic and covalent bonding. These technical ceramic materials are produced by sintering a powder, often at high-temperature and high-pressure. In the past 10 years, interest in high temperature structural ceramics has led to a search for starting materials with ideal properties for the production of high quality ceramic components. It has been proposed that spherical and submicron particles are the best to produce the desired material.

One of the most promising structural materials is silicon nitride. It has high strength over a wide temperature range, good thermal shock resistance, and strong wear and corrosion resistance. It is suitable for use in engine components, metallurgical and chemical plant components, wear-resistant parts and cutting tools. However, silicon nitride is very difficult to sinter, mainly due to the lack of a liquid phase and to its strong covalent bond structure. In addition, it requires high-purity, submicron and preferably crystalline powder (Saito, 1988).

Powder control is thus very important in controlling the quality of the ceramics (Nicholson, 1988). The free energy of sintering must be large and negative, which corresponds to a reduction of the system surface area. Hence, there is a requirement for powders with high surface area. Also important for sinterability is the number of particle contacts per unit volume and the void space should be as small as possible. The classic view is that monosized spherical particles are ideal although suitable mixtures of different particle sizes can reduce the void space further, but cause problems in achieving homogeneous mixing. Recently Messing (1992) stated that a slight degree of polydispersity gives a better packing of the particles, thus improving the sinterability. It is clear that agglomerated particles also deteriorate the sinterability of the powder because of the packing problem. This can lead to micro-cracks in the sintered material. The development of "hard" locations in the material which shrink slower than the surrounding structure leads to undesired stresses. Absolute chemical purity of the powders is also essential since trace impurities tend to concentrate at the grain boundary, thus preventing easy sintering.

A special kind of aerosol reactor is the Laser-Chemical Vapor Precipitation (L-CVP)

reactor, initially developed at MIT (Cannon *et al.*, 1982). Characteristic of this reactor is the very fast heating (ca. 10^6 K/s) of one or more of the gaseous reactants by means of matching the frequency of a high-powered laser to the molecular frequency of the gas. The molecules thus heated distribute the heat by collisions with other molecules. This leads to rapid nucleation of very small aerosol particles and coagulation into larger particles. The actual reaction zone is a flame with a high temperature although without oxygen and not self-sustaining. The advantage of this reactor over a conventional furnace is the absence of a surface, which decreases the rate of homogeneous nucleation and introduces impurities into the powder. The process has a low specific energy content because the carrier gas is not heated and is, therefore, more energy-efficient. Here, SiH₄ is utilized as absorbing reactant. The explosivity of pure SiH₄ in contact with O₂ further discourages the use of a furnace whilst in the L-CVP reactor the SiH₄ flow is surrounded by a large flow of inert carrier gas. The particles emitting from the flame are rapidly cooled by this inert gas. SiH₄ (silane) decomposes above about 800 K into Si (silicon) and H₂ (hydrogen):

$$SiH_4 \Rightarrow Si(1 \text{ or } s) + 2 H_2$$

Reaction with NH₃ (ammonia) leads to the formation of Si₃N₄ (silicon nitride):

$$3 \operatorname{SiH}_4 + 4 \operatorname{NH}_3 \Rightarrow \operatorname{Si}_3 \operatorname{N}_4 + 12 \operatorname{H}_2$$

The scope of this work is to reach a more fundamental insight into the processes taking place in the reactor. Therefore, the different stages in the particle formation process are investigated theoretically and are used in the design of a new reactor. Synthesis experiments are described and are investigated using a thermophoretically sampling system.

Using CVD Phase Diagrams to Understand Particle Formation

Thermodynamic calculations are a useful tool in understanding a specific CVD system and in optimizing the process conditions. A thermodynamic analysis must be completed before the kinetic effects are considered. Furthermore, kinetic models often include a thermodynamic term. In the case of homogeneous nucleation of ceramic powders, the supersaturation which is the driving force for the process must be known. Being interested in Si_3N_4 formation both from SiH₄ and chlorinated silanes which are economically more attractive (Bauer et al., 1991), the Si-H-Cl-N system has to be considered. A detailed thermodynamic analysis is given by Kruis et al. (1992). The result of this work is presented in the form of CVD phase diagrams, depicting which solid phases would deposit as a function of the experimental variables such as temperature and the input gases. These diagrams give phase boundaries and also the conversion ratio of the Si_3N_4 and Si phases, which is defined as the ratio of number of moles silicon deposited in the form of liquid or solid Si or Si_3N_4 and the total input number of moles silicon. These CVD phase diagrams, with the full range of silane gases, extended toward high temperatures and including the effects of pressure variation and H₂ or N₂ dilution, can be useful to optimize process conditions and in selecting a particular synthesis path.

An example is shown in Figure 1, for the SiHCl₃/NH₃ system at 1 bar. When premixing the SiHCl₃ and NH₃, the low-temperature formation of polymeric solid products like silicon diimide (Si(NH)₂), present a problem, because of deteriorating the Si₃N₄ quality and clogging of the nozzles. This is shown as path 1 in the figure. This problem can be

solved by using a two-stage reactor: first heating the silane gas, without NH_3 present, and then adding the NH_3 . Then there are two possibilities. The Si_3N_4 can be directly formed out of a no-condensed-phase (n.c.p.) region by homogeneous nucleation, probably via gaseous precursors like SiN and Si_2N (path 2 in Figure 1). The second possibility is that liquid Si particles are formed by homogeneous nucleation coming out of the no-condensed-phase region. The small Si nuclei grow by coalescence of liquid drops and then these Si particles come in contact with NH_3 and react (path 3 in Figure 1) into solid Si_3N_4 . It is clear that the morphology of the particles formed in these different ways will also be different.



Figure 1. CVD phase diagram of the SiHCl₃/NH₃ system at 1 bar, including contours of constant conversion ratio. The possible routes of forming Si_3N_4 are indicated: from an imide region (1), a silicon region (3) or from the gas phase (2)

Homogeneous Nucleation of Silicon

Particle formation by homogeneous nucleation from the gas-phase is an important phenomenon both in particle synthesis from the gas phase (Chemical Vapour Precipitation, CVP) and heterogeneous deposition (Chemical Vapour Deposition, CVD). In CVD processes, especially the manufacture of microelectronic devices, the formation of particles must be avoided whilst in the Laser-CVP process homogeneous nucleation is the essential step through which the ceramic powder is formed. An understanding and quantitative description of this process is, therefore, necessary. In research on the Laser-CVP process of Si_3N_4 (Bauer, 1991), SiH_4 was replaced by the chlorinated silanes SiH_2Cl_2 , $SiHCl_3$, and $SiCl_4$. The experimental results revealed that pure SiH_2Cl_2 does nucleate at high temperatures but $SiHCl_3$ and $SiCl_4$ do not. One of the purposes of this work is to investigate the conversion ratio, the nucleation potential and the nucleation rate of SiH_4 and of the chlorinated silanes. Unfortunately, the prediction of nucleation model was therefore checked by using reported experiments, and the assumptions inherent to the model were tested.

The classical nucleation theory is the most common approach for treating a supersaturated system. However, it results often in being a factor of 10^3 to 10^7 lower than

experiments. Katz and Widersich (1977) recognized that use of the equilibrium cluster size distribution is not correct and gave a kinetic description of the nucleation process. They included an unevaluated normalization constant in their final expression. Girshick et al. (1990) suggested an evaluation of this normalization constant by requiring that the equation describing the pseudoequilibrium number concentration be satisfied for monomers, resulting in an enhancement of the classical nucleation rate by a factor of $(exp(\Theta))/S$, in which the dimensionless surface tension Θ is defined by $\sigma s_1/(k,T)$. σ is the surface tension of the condensed species and s_1 is the surface area of a monomer. As a result, the kinetic expression for the nucleation rate is 10³ to 10⁶ times larger than the classical thermodynamic expression, which seems more in agreement with reported experiments.

The supersaturation of the silanes in H2 dilution was calculated using the chemical equilibrium program SOLGASMIX. It is important that both p and p, are calculated in this way. Another important parameter is the surface tension, because the nucleation rate is a very strong function of the surface tension. Here experimental values for both liquid and solid silicon were taken from literature (Mezev and Giber, 1982, Levin et al., 1966) and interpolated. Calculations of the nucleation potential showed that this parameter indicated the largest driving force for particle formation at lower temperature. As this is in contradiction with experimental observations, it was concluded that this parameter, which is often used in CVD to study particle formation, is not useful in screening the gases for their nucleation potential.

Calculations for the nucleation rate were made, using both the classical model and the kinetic model. Experimental data from literature on the onset of nucleation (Eversteijn, 1971, Herrick and Woodruff, 1984) were used to verify the models. In Figure 2 an example is shown, the SiH₄/H₂ system. It is concluded that the kinetic model from Girshick et al. (1990) agrees the best with the experimental results. A complete description of the results is shown by Kruis and Scarlett (1993).





E

Aggregate Formation and Sintering

In order to describe the evolution of the particle size in systems where particle growth by sintering of particles is possible, a simple monodisperse model describing the aggregation and sintering was developed (Kruis *et al.*,1993). In this model, the concept of Koch and Friedlander (1990) to describe the change in surface area of an aggregate by sintering was used. By solving a set of equations for the number concentration of aggregates, the surface area of an individual aggregate and the volume of an aggregate, the primary particle size and the number of primary particles in an aggregate can be determined. In order to account for the enhanced collision cross section of aggregates, the relation given by Matsoukas and Friedlander (1991) was used. Furthermore, the model can be used over the whole particle size range by using the Fuchs expression. The aggregates are assumed to be fractal.

After an evaluation of the sinter mechanisms of silicon, grain boundary diffusion appeared to be the most important mechanism for sintering of submicron silicon particles, closely followed by surface diffusion. The structure-dependent monodisperse model was evaluated by comparing it with a detailed two-dimensional sectional model (Xiong and Pratsinis,1993). As an example, the model is applied to the laser-synthesis of silicon particles, described in another section of this article. The measured centre-line temperature profile is described using a linear increase and decrease, shown in Figure 3 together with the evolution of the primary particle size calculated using the model. Also shown in the figure is the effect of a lower temperature and dilution with N_2 , characteristic for the outer boundaries of the flame, which clearly leads to a smaller primary particle size. As the melting point of silicon is 1680 K, it is clear that particle growth below the melting point by solid state sintering mechanisms is possible.



Figure 3. The primary particle size and the temperature profile in the centre of the flame (solid lines) and at the flame boundary (broken lines) as a function of time according to the aggregation/sinter model.

Characterization of Aggregates and Agglomerates Using Image Analysis

Because of the extremely high number densities in the laser-heated flame, it will be difficult to prevent aggregation. In general, aggregated and agglomerated particles are found in systems where high number densities occur or where the collection mechanism concentrates the particles onto a surface. The automated analysis of photographs or images of these particles is complicated by the fact that image analysis programs for particle size analysis consider contacting particles being one, while the primary particle size is often the most important parameter looked for and cannot be obtained with the standard programs. Therefore, a new method has been developed which is capable of locating circular objects in an image, even when these objects are overlapping with each other or when only a part of the circle contour is present.

This method, which is based on the Hough Transform (Ballard and Brown, 1982) and is called the Sparse Hough Transform, first locates the circle contours, the 'edges', by applying standard image analysis routines. Then possible circle centres are searched for using a so-called distance transform (Borgefors, 1986), which can be seen as a method to 'peel off' several layers of pixels from the particles. The Hough transform is applied, which determines the percentage of edge pixels corresponding to a circle for each possible circle centre and each possible radius looked for. Then, by interactively changing the minimum percentage needed for detecting a circle and visually controlling the results by comparing the circles found with original image, a distribution of primary particle sizes can be obtained. The method was tested on a number of test images and was shown to work well. An example is given in Figure 4. The program was also applied to a number of TEM photographs containing aggregated and agglomerated particles, produced by the L-CVP process.






Figure 4. Example of Sparse Hough Transformation on test image: (A) grey level test image, (B) edge detection, and the grey area indicating possible circle centres as a result of thresholding the distance transform, and (C) circles recognized.

The structure of agglomerates can be determined also from image analysis methods. The agglomerates can be characterized using a fractal dimension (see for a description of several methods Cleary *et al.*, 1990). In this work, the density-density correlation function was adopted to obtain this fractal dimension, which has the advantage that each agglomerate can be characterized with a fractal dimension, even agglomerates containing few primary particles. The disadvantage of this method is its computational burden, but this can be solved by reduction of the original image. Another common problem of this method is the fact that

(B)

(C)

the correlation function deviates more and more from the straight line necessary to obtain the fractal dimension when the radius of gyration is approached, making the fractal dimension a strong function of the range fitted. This can be minimized by fitting the correlation function to a so-called cut-off function, stemming from aggregate description in colloid science (Lin *et al.*, 1990), which uses an exponential decaying function to fit the density-density correlation function. This was done for 21 agglomerates produced in the L-CVP process, and the result is shown in Figure 5. The mean fractal dimension found is 1.59.



Figure 5. (A) Distribution of fractal dimensions of the 21 recorded agglomerates, (B) Fit of the density-density correlation function C(r), averaged over 21 agglomerates, to the simple exponential cut-off function, giving a fractal dimension of 1.59.

Experimental Set-Up of the Laser-CVP reactor

In the preceding section it was shown that the way the reactants are mixed is important. Formation of $Si(NH)_2$ at low temperatures has to be avoided because of undesirable clogging of the nozzles and deterioration of the powder. Aoki *et al.* (1988) also showed that premixing of SiH_4 and NH_3 results in extremely small particles, ca. 8 nm, so they developed the injection-mixing L-CVP reactor, also used by Bauer (1991). A laminar mixing system was devised in our work, in order to overcome experimental difficulties with a turbulent flame, such as unreliable sampling and temperature measurements, and deterioration of the laser entrance windows by particles swept away from the flame.

The newly developed laminar coaxial mixing system enables the controlled mixing of the reactants. The system consists of 4 concentric nozzles, Figure 6. The source gas (e.g. the SiH₄) and the reactant (e.g. the NH₃) flow through the first and the third nozzle. These two flows are prevented from mixing with each other by means of the inert sheath gas coming from the second nozzle (e.g. H₂ or N₂). The basic idea of this system is that the meeting point of the first and the third gas can be controlled by the velocity of the second.



Figure 6. Schematic diagram of the nozzle system. The mixing of the gases 1 and 3 can be controlled by varying the flow of the sheath gas 2.

With velocities between 0.5 and 5 m/s, the meeting point of the SiH_4 and NH_3 can be, taking into account a diffusion time of 0.6 ms calculated using standard penetration theory, between 0.3 and 3 mm above the first point of laminar mixing. This means that it is possible to mix

 SiH_4 and NH_3 either before or in the laser beam. The fourth nozzle provides the carrier gas, N_2 , which transports away the powders produced without causing deposition on the walls or the windows. The small dimensions of the three inner nozzles required a special construction in order to be able to remove them individually. Each of the nozzles consisted of a stainless steel needle which was mounted on a larger holder. Each nozzle holder fits onto a screw tapping into the reactor base. In this way, a very flexible system is created, because the individual nozzles can easily be left out or changed. For example, for Si synthesis the mixing system is not necessary and the first and second nozzles can be left out, resulting in a larger diameter inner nozzle.

The complete reactor system consists of a gas control unit, a CO₂ laser, a reactor, a powder collection unit, a two-colour pyrometer and a sampling system. A tunable 200-W continuous CO, laser (Edinburgh Instruments PL6, Edinburgh, UK) radiating at a wavelength of 10.60 µm (the 10P20 line) was focused with a ZnSe lens (focal length : 30 cm) to a spot 1.5 mm in diameter centred above the inner nozzle. The laser enters and leaves the stainlesssteel reactor system through ZnSe windows located at the end of two small tubes. Two large diameter (10 cm) quartz windows in the reactor enable the visual observation of the flame and temperature measurements by means of a two-color pyrometer (Bauer 1991). In order to be able to change the position of the laser beam, the whole reactor was mounted on a x-yz-r table. The gas and particle stream exiting from the flame flowed through a tubular funnel to stabilize the flame and was connected to an electrostatic precipitator operating between 5 and 10 kV and 0.2 to 0.5 mA. The pyrex collection tube could be closed by two large valves and brought into a glove box without oxidizing the powder. Possible unreacted SiH, was removed in a furnace behind the collection system. All experiments were carried out at atmospheric pressure, but with a valve and a pump system the reactor could be evacuated in order to remove the air after the system was opened. The gas control system consists of a series of mass flow controllers (MKS Instruments 1259B and 147B, Munchen, Germany) and safety valves coupled to a pressure transducer (MKS Instruments) and an emergency button. The gas flasks were placed in a gas cabinet (Air Products Nederland B.V., Waddinxveen, The Netherlands) for safety reasons.

Because of difficulties inherent to light scattering methods, experimental investigation of particle formation was carried out using thermophoretic sampling. In this technique, a cold surface is moved through the flame, and because of the thermophoretic force which is in the direction of decreasing temperature the particles are captured on the surface. The advantage of this technique is that the particles captured can be characterized also on their morphology. and that chemical and crystallographic methods can be applied onto the particles. The use of thermophoretic sampling in the L-CVP reactor must overcome specific problems like the small dimensions of the flame, the high temperatures, the extremely high number concentrations and the closed high purity gas reactor system. Besides, the particles have to be captured onto a standard TEM grid because of the nanometre size scale of the particles. Therefore, a device was constructed which consists of a pneumatically controlled probe which holds a small tube with a slid at the end where a rectangular TEM grid (1 x 3 mm) can be held with a small screw. In this way the TEM grid can be moved quickly through the flame, while the probe moves along the flame. To avoid exposure to the air, the sampling apparatus was fitted in a chamber separated from the reactor system by a large gate-valve and connected to a vacuum-pump and a N₂ purge. The vertical and horizontal position of the probe can be changed to be able to take samples from different positions from the flame.

All powders synthesized were handled in a glove box filled with Ar and free of water and oxygen. The particle size and morphology were determined by a transmission electron microscope (Philips EM400, Eindhoven, The Netherlands). The powders were analyzed using IR spectroscopy, X-ray diffraction and BET surface area. The N-content of the powders was determined by decomposing the samples into LiOH at 950 K and then conductometrically measuring the amount of NH₃ released (Bauer, 1991).

Experimental Results

Silicon Synthesis

The synthesis of silicon is of interest because of its promising role as a starting powder in the production of RBSN (Reaction Bonded Silicon Nitride). Besides, it shows some characteristics of the L-CVP reactor. In order to produce silicon in this reactor, SiH₄ flows from the first nozzle with a inner diameter of 0.7 mm, surrounded by a low-velocity N₂ stream. When the laser beam (150 W, 10P20 line) with a diameter of 1.5 mm is directed to a point 2 mm above the nozzle, a stable luminescent flame with a base of 2.5 mm in diameter is formed. Two-colour pyrometry revealed that the centreline temperature increases sharply until 2000 K and then gradually drops off, in accordance to the decrease in luminescence. When SiH₂Cl₂ is used as source gas, a maximum temperature of 1550 K is reached (Bauer, 1991), probably because the decomposition reaction of SiH₂Cl₂ is more endothermic than that of SiH₄. At the visual boundary of the flame, a temperature of ca. 500 K lower is observed, probably by dilution.

The particle formation process was investigated using the sampling apparatus. Samples taken from the position in the flame where the temperature is at its maximum (2000 K) show spherical, crystalline silicon particles with particle diameters between 35 and 70 nm. The particles appear to have been deposited below the melting point of silicon due to the cooling in the boundary laver around the grid since individual overlapping particles can be discerned. There is also a small number of agglomerates of smaller primary particles, 10-30 nm. These particles show sinter necks and no overlap. Samples taken higher in the flame at lower temperature, ca. 1350 K, contain particles which are more agglomerated and where sintering has clearly taken place, also now in the case of the larger particles. The number of primary particles per agglomerate has clearly increased and the polydispersity decreased. The agglomerates of smaller primary particles are also present. Samples taken above the flame show no clear difference to those from the middle sample point except that there are almost no agglomerates comprising only a few primary particles. In most cases the primary particles in an aggregate are approximately of the same size. The aggregation/sinter model can be used to describe the evolution of the primary particle size and also explains clearly that the aggregates containing the smaller particles are formed at the outside of the flame, where the temperature is lower (Kruis et al., 1993).

In order to produce larger particles, a larger inner nozzle diameter (2.4 mm) was used, resulting in a lower velocity and a higher residence time. In Figure 7 an example is shown of the particles produced. A mixture of perfectly spherical Si particles, up to several hundreds of nanometres in diameter, together with smaller, more aggregated and sintered particles can be seen. This accords with the sinter model, as a 10 nm particle sinters 10⁴ times as fast as a 100 nm particle. Sampling experiments where samples where taken from the visual boundaries of the flame showed small, aggregated particles while the large, spherical particles are absent. Therefore it can be concluded that the large particles are formed by coagulation at a temperature above the melting point of silicon, while the small, aggregated particles are formed by aggregation and sintering below the melting point at the outer boundaries of the flame.



Figure 7. Example of silicon particles with different morphology found in SiH₄ decomposition.

Silicon Nitride Synthesis

The controlled synthesis of Si_3N_4 is of interest because the formation mechanisms are not yet fully understood. A better understanding would facilitate the commercial exploration of the system. In order to characterize the L-CVP reactor, three process variables were varied: (1) dilution of the SiH₄ with H₂, (2) varying the flow rate of the sheath gas, and thereby controlling the mixing between SiH₄ and NH₃, and (3) changing the diameter of the laser beam. The configuration used in all the experiments consisted of the 4 nozzles, from which starting from the central nozzle, respectively, the SiH₄, sometimes diluted with H₂, the N₂ as a sheath gas, the NH₃, and the N₂ carrier gas were metered. The laser diameter was usually 1.5 mm. The laser was tuned to the 10P20 line and operated at its maximum power, i.e. 150 W. The gas flows were such that the velocities of the SiH₄, the N₂ and the NH₃ emerging from the three nozzles are roughly equal (80 sccm SiH₄, 160 sccm N₂ and 320 sccm NH₃).

The flame appeared to be not turbulent and very stable, and there was no particle deposition in the reactor. In comparison to the SiH_4 decomposition flame, the SiH_4/NH_3 flame is brighter and has a whiter colour. This is in accordance with the temperature measurements, which show higher temperatures, even as high as 3000 K in some cases. The higher temperatures might be caused by absorption by the Si_3N_4 particles and by absorption by the NH₃. Decreasing the sheath gas flow has the most profound effect: the lower the sheath gas flow, the higher the temperature.

The particles produced were studied by TEM. Three kinds of particles could be discerned in almost all powders: (1) extremely small, aggregated, amorphous, needle-like particles with diameters between 2 and 4 nm (Figure 8A), (2) amorphous, aggregated, approximately spherical particles with diameters between 10 and 30 nm (Figure 8B), and (3) large crystalline particles of irregular form with sizes between 30 and 150 nm (Figure 8C).



Figure 8. Example of the three types of particles found: (A) small, fibre-like particles, (B) heavily aggregated particles, and (C) large, irregular, crystalline particles.

Increasing the diameter of the laser beam has the most profound effect. This decreases the amount of small fibres and of the smaller, aggregated amorphous particles whilst the number of large crystalline particles increases. The morphology of the crystalline particles also

changes, the particles become more edgy, more rectangular and faceted. This is consistent with the results of the X-ray analysis which showed this powder to be composed mainly of crystalline α - and β -Si₃N₄, while in all other powders the only crystalline particles were silicon particles. This can be explained by the purity of the powder, described in the next section.

The purity of the Si₃N₄ is an important experimental result. Pure Si₃N₄ has a Ncontent of 40 w%, while in most powders the N-content will be lower due to silicon contamination. The specific surface area can be used as an indication of the particle size. In Figure 9 both experimental results are shown as a function of the three process parameters varied. Decreasing the concentration of SiH4 in H2, Figure 9A, increases the specific surface area. This can be explained by the lower silicon concentration, resulting in a smaller particle size and thus a higher specific surface area. As the Si_3N_4 formation proceeds via the Si path because the high sheath gas velocity prevents fast mixing between SiH₄ and NH₃, this results then in a higher N-content, also found experimentally, because smaller Si particles are nitrified easier. Decreasing the sheath gas flow results in a lower specific surface area, Figure 9B. Temperature measurements revealed that the temperature of the flame increases sharply with decreasing sheath gas flow, from a maximum of ca. 2100 to 3000 K. This is probably due to the transition from Si₃N₄ via Si to Si₃N₄ formation directly from the gasphase, also indicated by the higher N-content. The Si₃N₄ particles then can decrease their surface area by sintering mechanisms. The higher the temperature, the faster the sintering and this explains the decreasing surface area with decreasing sheath gas flow. The last experimental parameter varied finally produced almost pure Si3N4: increasing the diameter of the laser beam does not have a marked effect on the surface area, Figure 9C, but it has a positive effect on the Si₃N₄ purity. Probably a more uniform heating of the reactants, as the NH₃ is now also heated, and a decreased beam intensity account for this effect. X-ray diffraction indicated that the powder produced with a low sheath gas velocity and a broad laser beam contains almost exclusively α - and β -Si₃N₄. It seems that crystallization of Si₃N₄ is favoured by the Si₃N₄ being relatively pure.



(B)

(A)

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Figure 9. N-content and specific surface area as a function of: (A) % SiH₄ in H₂ (100 sccm SiH₄+H₂, 200 sccm N_2 sheath gas, 320 sccm NH₃), (B) flow rate of N_2 sheath gas (80 sccm SiH₄, 320 sccm NH₃), and (C) laser beam diameter (80 sccm SiH₄, 40 sccm N_2 sheath gas, 320 sccm NH₃).

The thermophoretic sampling apparatus proved the existence of two synthesis paths. Sampling showed that when operating with a high sheath gas velocity low in the flame a mixture of spherical Si particles and amorphous Si_3N_4 was formed. Higher in the flame, when the NH₃ reaches the inner flow, the Si is partially transformed into Si_3N_4 , yielding irregular or wedge-shaped particles. However, complete nitridation was not obtained and crystalline Si was detected in the powder produced. When using a low sheath gas velocity and an increased laser beam diameter, small amorphous Si_3N_4 particles were formed low in the flame due to more rapid mixing between the SiH₄ and NH₃. Higher in the flame the particles become larger, probably caused by sintering since Si_3N_4 has no liquid phase, and crystallinity develops. Above the flame faceted, rectangular particles of α - and β -Si₃N₄ were formed during the cooling of the process stream.

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Measurement of Ultrafine Particles



MINIMIZATION OF THE DIFFUSIVE BROADENING OF ULTRAFINE PARTICLES IN DIFFERENTIAL MOBILITY ANALYZERS

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Analysis of diffusion effects in DMAs in the limit of high Peclet number shows that diffusional broadening may be minimized when the separation between entrance and exit slits is comparable to the inter-electrode gap. This prediction is verified in a short version of Reischl's DMA using molecular ions from an electrospray source.

1. INTRODUCTION

Differential mobility analyzers (DMAs) are widely used to measure aerosol size distributions and to extract submicron monodisperse particles from polydisperse aerosols (Knutson and Whitby, 1975; Liu and Pui, 1974; Reischl, 1991). In the ultrafine region, however, their response is influenced by diffusion, and they no longer function as monodisperse aerosol generators. The effect of Brownian motion on DMA performance has been studied theoretically and experimentally by Stolzemburg (1988; see his review of earlier work), who shows that this phenomenon severely limits resolution for particles smaller than 10nm. The basic question addressed here is, could geometrical and fluid dynamical optimization of the instrument yield high resolution at mobilities near 1cm²V⁻¹s⁻¹? Analysis in the large Reynolds number limit yields a positive answer, but only provided that (i) the axial distance between the aerosol entrance and the exit slits are comparable to their radial separation, and (ii) the instrument 's Reynolds number is of the order of 1000.

An important stumbling block in an experimental program of improving the performance of DMAs in the nanometer range has been the lack of procedures to generate monodisperse calibration aerosols. The reason is that the only well established source for such small particles with a narrow size distribution is a DMA, but existing DMAs do not produce monodisperse nanoparticles due to diffusive broadening. Stolzemburg has used theory to account for such diffusive broadening in the source aerosol, and then verified the theory through measurements of the additional broadening caused by a second DMA. The more direct approach followed here uses molecular ions as the "monodisperse" mobility standard. This method is conceptually straightforward, but faces technical difficulties which appeared as most challenging until recently. First, the problem that commercially available aerosol DMA's show no peaks in the range of ionic mobilities, has been elegantly solved by Schmidt-Ott and Kutz in 1990. A second obstacle is associated to the fact that most ion-producing schemes lead to a complex series of reactions, whose end product is a mixture of ions with several mobilities, which are not easily resolved from each other in DMAs. Furthermore, ions are typically produced from volatile precursors, which tend to absorb on the instrument's walls, remaining there as long term contaminants. The solution to this problem in ion mobility analyzers has been to keep the instrument at relatively high temperatures. Our somewhat simpler approach follows from the recent work of Fenn et al. (1989), which has established electrospray ionization as an ideal source of ions of involatile species, often highly "monodisperse". Ion mobility analyzers have been used for a long time, and have reached a high degree of sophistication (McDaniel & Mason, 1973; Von Helden et al., 1991). Modern instruments tend to be of the time-of-flight type, far removed from their aerosol cousins. However, one of their earlier embodiments, the Erikson tube (Chapman, 1937), is conceptually quite similar to Whitby's or Reischl's aerosol DMAs, as illustrated in the recent work of Strydom et al. (1990). The differences between the ion and the aerosol instruments are nonetheless substantial, and no attempt to review the former will be made here. Our main interest is not to use aerosol instruments to measure ion mobilities, but to extend the range of current aerosol DMAs into the nanometer range through modifications as minimal as possible. The structure of this paper is the following: The theory of diffusion effects in DMAs is first sketched in a fashion more mathematically compact and generalizable (but less physically inspired) than Stolzemburg's, to find the optimal DMA length. We then describe the experimental scheme and tests through which molecular ions are used to confirm these theoretical conclusions on a modified version of one of Reischl's instruments.

2. THEORY OF DIFFUSION IN DMAs

We assume that the particle velocity field in the annular space between two coaxial cylindrical electrodes with radii R_2 and R_1 ($R_2 > R_1$) is given by

$$\mathbf{u} = \mathbf{u}(\mathbf{r}) \, \mathbf{e}_{\mathbf{x}} - Z \, \mathbf{E}(\mathbf{r}) \, \mathbf{e}_{\mathbf{r}}; \qquad Z = qD/(kT)$$
(1, 2)

where r and x are the radial and axial cylindrical coordinates, and the e_i are the corresponding unit vectors. $u(r)e_x$ and $E(r)e_r$ are the fluid velocity and electric field, both assumed independent of x and with no radial and axial components, respectively. Z is the particle mobility, q its charge, and D its diffusion coefficient. T is the absolute temperature of the gas, and k is Boltzmann's constant. We assume that charged particles are injected axisymmetrically at z = 0 at the outer electrode $r = R_2$, and that they move inwards (qE > 0). For a cylindrical geometry, E takes its purely radial asymptote shortly downstream the entrance slit, given by

$$E = \gamma/r; \qquad \gamma = V/\ln(R_2/R_1), \qquad (3)$$

4)

in terms of the voltage difference V between the outer and the inner electrode. The fluid velocity would also eventually reach the "viscous" asymptote

$$u = U v(y); v(y) = ag(y); g(y) = \frac{1-y^2}{1-y_1^2} - \frac{\ln y}{\ln y_1}; y = \frac{r}{R_2}; y_1 = \frac{R_1}{R_2},$$
 (5-8a,b)

where the proportionality constant a in (6) is chosen such that U in (5) is the average velocity

$$U = Q/[\pi(R_2^2 - R_1^2)]$$
(9)

based on the flow rate Q and the cross section. Accordingly,

$$\int_{y_1}^{1} y v(y) dy = \frac{1 - y_1^2}{2}; \quad a = \frac{1 - y_1^2}{2F_2(y_1)}; \quad F_2(y_1) = \int_{y_1}^{1} y g(y) dy. \quad (10-12)$$

However, if the Reynolds number defined as (v is the kinematic viscosity of the gas)

$$Re = Q/[\pi v(R_1 + R_2)]$$
(13)

is a large quantity, and the axial length of the instrument is not many times R_1 - R_2 , v(y) may be quite different from (6), and may even be approximated by the inviscid form

$$v_i(y) = 1.$$
 (14)

In the absence of diffusion, particle trajectories are defined by a null value of the "streamfunction" η , and an axial position L at which ions of a certain mobility hit the inner electrode:

$$\eta(x, r) = x + \int_{R_2}^{r} \frac{ru(r) dr}{Z\gamma}, \quad L = \int_{R_1}^{R_2} \frac{ru(r) dr}{Z\gamma} = \frac{Q}{2\pi Z\gamma}.$$
 (15, 16)

When D = 0, if the particle's spatial distribution n(r, x) is infinitely narrow at $r = R_2$,

$$n(x, R_2) = \delta(x) \tag{17}$$

(δ is the Dirac's distribution), it will remain undispersed throughout so that $n(x, r) = \delta(\eta)$. However, diffusion changes the picture, and the evolution of n must be described through

$$\mathbf{u}.\nabla \mathbf{n} = \mathbf{D}\,\nabla^2 \mathbf{n}.\tag{18}$$

Let us now consider (18) in the limit Re >> 1, with (17) as initial condition and boundary conditions of vanishing n at large distances upstream and downstream from the injection port. Then, diffusion effects are slight, even when $D \sim v$, and (18) may be solved asymptotically by the

method of subcharacteristics (Cole, 1968). Introducing η and r as new independent variables and ignoring $\partial^2/\partial r^2$ terms with respect to terms $\partial^2/\partial \eta^2$, one finds to lowest significant order in Pe:

$$\frac{-\gamma Z}{rD} \frac{\partial n}{\partial r} = \left[1 + \frac{(ru)^2}{(\gamma Z)^2}\right] \frac{\partial^2 n}{\partial \eta^2}; \quad Pe = \text{Re } v/D, \quad (19, 20)$$

where the Peclet number Pe is typically a few times Re, even for molecular ions. (19) becomes a simple diffusion equation in terms of the time-like variable s:

$$\frac{\partial n}{\partial s} = \frac{\partial^2 n}{\partial \eta^2}; \qquad s(r) = \int_{r}^{R_2} \frac{D}{\gamma Z} \left[1 + \frac{(ru)^2}{(\gamma Z)^2} \right] r dr , \qquad (21, 22)$$

whose solution for the simplest initial conditions (17) is

 $n \sim s^{-1/2} \exp[-\eta^2/(4s)].$ (23)

If the aerosol flow out is small, the sampled aerosol concentration is simply given by (23) particularized for $r = R_1$ and $x = L_0$, where L_0 is the distance between the exit and the entrance slits:

$$n_{out} \sim s_1^{1/2} \exp[-(L-L_0)^2/(4s_1)].$$
 (24)

 $s_1=s(R_1)$ may be written in terms of the characteristic length L* and the function $G(y_1)$ of R_1/R_2 as

$$s_{1} = \frac{G(y_{1})L^{2}}{Pe} \left[\frac{L^{*}}{L} + \frac{L}{L^{*}} \right]; \quad G^{2}(y_{1}) = \frac{8}{(1+y_{1})^{3}(1-y_{1})} \int_{y_{1}}^{y_{1}} g^{2}(y)y^{3}dy; \quad L^{*} = \frac{R_{2}-R_{1}}{G(y_{1})}. \quad (25-27)$$

Introducing finally the dimensionless DMA voltage ψ and length b, we find

$$n_{out} \sim \frac{\psi}{\sqrt{[(b/\psi) + (\psi/b)]}} \exp\left[\frac{-\text{Pe}(\psi-1)^2}{4[(b/\psi) + (\psi/b)]G(y_1)}\right]; \quad \psi = \frac{L_0}{L}; \quad b = \frac{L_0}{L^*}.$$
 (28-30)

The function $G(y_1)$ depends on the ratio of radii y_1 , and on the flow field v(y), but departs little from unity for most cases of practical interest. For a flat velocity profile, with v=1, $G(y_1) = [2(1+y_1^2)]^{1/2}/(1+y_1)$, which is unity for a narrow gap $(x_1 \rightarrow 1)$, and 1.009 for $y_1 = 0.757$ (Reischl's DMA). For the case of viscous flows considered in (5-8), $G(y_1)$ is given in the following table:

$1/G(y_1)$	0.9129	0.9125	0.9114	0.9104	0.9055	0.8918	0.8654
Y1	1.	0.9	0.8	0.755	0.6	0.4	0.2

The length L^{*} introduced in (27) can be readily interpreted as the optimal value for the distance L₀ between inlet and outlet slits in the limit of Pe >> 1. In this case, the exponential term in (28) drops very rapidly to zero when ψ departs slightly from unity, so that

$$n_{out} \sim \exp\left[\frac{-\text{Pe}(\psi-1)^2}{4(b+b^{-1})G(y_1)}\right]$$
, when $\frac{\text{Pe}}{4(b+b^{-1})} >>1.$ (31)

n is thus nearly Gaussian in the dimensionless DMA voltage ψ , with a variance proportional to $\sqrt{[b+b^{-1}]}$. Diffusive broadening is therefore minimized at b=1, thus, for a DMA length near R₂-R₁:

$$(L_0)_{optimal} = L^* = (R_2 - R_1)/G(y_1).$$
 (32)

The predicted consequences of operating at lengths larger than L^{*} are shown in figure 1 for 4G/Pe = 0.003 (Pe/G = 1333), and values of b between 1 and 30. The representation of $n(\psi)$ from (28) corresponds to the flux of particles through the extraction slit as a function of the dimensionless

DMA voltage for the case of a strictly monodisperse aerosol (constant Z). These curves thus represent the diffusion-broadened mobility spectra of a monodisperse aerosol for the realistic conditions Re = 333, G=1, v/D = 4. Notice first that there is only a slight increase in the width of the curves when b rises from 1 to 3. This initial insensitivity is the obvious result of the fact that the variance is an extremum at b=1. Varying b from 1 to 2 increases the width only by 12% above the minimum. On the other hand, the resolution has already deteriorated substantially at b = 10, and quite dramatically at b = 30. Another interesting effect shown in figure 1 is that the maximum of the distribution is shifted noticeably to the right of unity for b = 30. To first approximation in the small quantity $\varepsilon = 4G/Pe$, the position ψ_m at which n is a maximum is given by

$$\psi_{\rm m} = 1 + \varepsilon \,(3b + 1/b)/4 + 0(\varepsilon^2). \tag{33}$$

In conclusion, in a DMA of optimal length operated laminarly at Re = 2000, the predicted mobility spectrum of an ionic species with v/D=6 would have a full width at half maximum of only 4.3%.

Notice finally that the distribution $n(\psi)$ used in this analysis is valid in the limit when the total gas flow down the annulus is much larger than the aerosol flow, so that the mobility spread is dominantly diffusive. In practice, the particles are introduced with a finite initial spatial width associated with a finite aerosol flow rate, so that n would result from a convolution of the initial distribution $n_0(x, R_2)$ with the fundamental solution (23). Likewise, a finite gas flow is drawn at the sampling slit, which takes particles from a finite set of streamlines (values of η). The extracted aerosol results thus from another convolution of $n(R_1, \eta)$ over the η variable at the inner electrode.

3. EXPERIMENTAL TECHNIQUE

In order to test the preceding theoretical predictions, the aerosol path inside a Reischl DMA (R2 = 3.30 cm; R1=2.50 cm) has been shortened by elevating the slit in the inner electrode, such that the inter-slit axial distance L_0 is only 1.6 cm (11.4 cm originally). This factor near two above the predicted optimum comes only at the expense of an expected 12% loss of resolution, and has the advantage of reducing the proportion of Lo occupied by the width of the two slits. This short DMA was first calibrated following Rader et al. (1986). A dioctyl phthalate aerosol was electrically classified in a TSI DMA (model 3071) and then fed into Reischl's DMA. The particle count rate at the exit of this second DMA was recorded versus its inner rod voltage V for Re in (13) between 125 and 410 (Q being the clean air flowrate). Peaks of the mobility distributions appeared within 2% of the ideal theoretical voltage. Such a close agreement was not expected a priori, for in the Reischl DMA the walls near the aerosol entrance slit depart from a cylindrical surface over a small but non-negligible fraction of the inter-slit region. Accordingly, the non-idealities in the geometry of the aerosol entrance can be neglected when comparing the DMA theory to the actual data. On the other hand, the widths of the calibration distributions measured were larger than expected in the limit of negligible diffusivity, because these calibrations required very small particles (between 20nm and 40nm in diameter), for which Brownian diffusion inside TSI's DMA may have been substantial (with the corresponding effect being much smaller inside the Reischl DMA).

In the experiments following these calibrations, the flow into the aerosol inlet of Reischl's DMA (kept at ground) was sampled from an electrospray source of molecular ions (Fenn et al., 1989). Aerosol fluxes out of the DMA were measured as a current, I, collected in an electrometer, as a function of the voltage V for a variety of flowrates of clean gas, Q, and at fixed flowrate of aerosol, qa. The flowrate of clean gas was kept equal to the flowrate of excess gas in the DMA. CO₂ was used for all of the flows, because this gas reduces the likelihood of electrical discharges in our electrospray source. The electrospray ions originate from a solution of NaOH in water (10mg/l). As the charged spray droplets evaporate, the electric field at their surface increases until they undergo Coulomb explosions. Eventually, this field becomes so high that solution ions start desorbing into the gas phase, and are then sampled into the DMA.

4. RESULTS

Figure 2 shows measured mobility distributions of the aerosol sampled from the electrospray at various clean gas flow rates Q in the DMA and at a fixed aerosol flow, qa=1.45 l/min. The voltage and current are normalized by their values at the maximum of the high mobility peak. The Peclet number (shown in the figure legend) has been defined based on the highest mobility, the total flowrate, Q+qa, and the assumption that the corresponding ions are singly charged. Three separate peaks can be resolved at the higher Peclet numbers, but they become wider at decreasing values of this parameter, until at Pe~500, maxima can hardly be recognized for the second and third peaks. Although the exact nature of the species from which these peaks originate is unknown, we believe that the one with the highest mobility corresponds to some form of molecular ion, probably a sodium ion surrounded by a stable hydration shell. It will be referred to as "the cluster peak". The stability of this cluster is confirmed by the fact that its mobility remains near 0.79cm²V⁻¹s⁻¹, quite insensitive to variations in the spray parameters and in the sampling flow rate. However, its width varied slightly with the conditions of the electrospray. The nature of the intermediate peak is unclear, though it is substantially wider than would correspond to an ion of the same mobility, and cannot therefore be a pure species. The mobility of the third peak varies widely with the electrospray condition, indicating that it is associated with the droplet's solid residues.

As shown in figure 3 at Pe=2700, the cluster peak follows approximately the expected trend, though with a measured distribution 30% wider than predicted. The disagreement can only be explained in part as due to a finite aerosol flowrate because the expected full width at half maximum in the absence of diffusion is $(q_a/Q) \le 2.6\%$. Our interpretation for the observed differences is that the cluster ion is not monodisperse, consisting instead of a core ion surrounded by n water molecules, where n is distributed around a certain mean value with nonzero variance.

As Pe is reduced, the effect of q_a on peak width cannot be ignored, and a correction is needed before comparing experiments and theory. If the initial distribution due to q_a were Gaussian, the square variances would be additive, so that one could write for the full widths at half maximum :

$$(\Delta V/V_{\rm p})^2 = (C q_{\rm a}/Q)^2 + 16 \ln 2 (b+b^{-1}) G(y_1)/Pe,$$
 (34)

where C is some empirical constant. The approximate validity of this hypothesis is confirmed in figure 4, which plots the measured $[Pe(\Delta V/V_p)]^2$ versus Pe for constant q_a and source conditions, which, according to the above equation, should be a straight line with a slope of 32.33 [G=1.099]. Instead, we obtain a slope of 43.4. The constant C takes the value 2.87, while one would have expected C = 1 for a monodisperse aerosol. This result points out again to the polydispersity of the source aerosol.

In conclusion, although the 30% disagreement between experiment and theory becomes worse at smaller values of Pe our measurements show unambiguously that a DMA of optimal length and high Reynolds number can "size" particles with high resolution down to the cluster region.

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CHARACTERIZATION OF ELECTROSPRAY-GENERATED NANOPARTICLES IN A HYPERSONIC IMPACTOR

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Use of small smooth collectors rather than porous frit surfaces improves substantially the resolution of hypersonic impactors sizing multiply charged nanoparticles. These result from the dry residue from an electrospray droplets, and are found to be monodisperse down to diameters of 5nm.

1. INTRODUCTION

For a long time since their development, the only aerosol instruments suitable for sizing particles smaller than 10 nm have been differential mobility analyzers (DMAs; Liu and Pui, 1974). However, inertial impactors operating with hypersonic jets (HIs) have also shown promise in this size range (Fernández de la Mora et al. 1990a). Interestingly enough, DMAs and HIs measure two independent particle properties, a feature which Hering and Stolzemburg (1993) have exploited to infer on-line the density of nanoparticles from combustion sources. Mobility is proportional to the charge q over the drag, while impactors infer mass over drag, so that both instruments in combination could also yield the unknown charge q and diameter dp of spherical particles of known density. Although ultrafine particles in the presence of thermal ions contain at most one elementary charge, q=e, q is often unknown and substantially larger than e, as in field charging, or photoelectric charging (Jung et al. 1988). In particular, the use of electrostatic atomizers (Cloupeau and Prunet-Foch, 1989) makes it possible to fragment liquids into highly charged droplets, even in the submicron range (Fernández de la Mora et al, 1990c; Meesters et. al, 1992), so that electrosprays may produce nanoparticles directly after evaporation of their rather small initial droplets into a solid residue. In these cases, the resulting aerosol is highly charged and cannot be sized through its electrical mobility only. Our current research on the production of monodisperse nanoparticles from electrosprays uses impactors to size highly charged particles with diameters between 20nm and a few nm. This work describes our progress in this direction.

Impactors are devices in which an aerosol jet collides perpendicularly against a flat surface or collector plate. In a well designed instrument, the plate acts as a low-pass filter which catches all particles larger than a critical diameter d* (the size cut), while allowing most smaller particles to remain in suspension. The essential feature leading to high sizing resolution is that the efficiency of capture varies very sharply from zero to one over a narrow range of diameters centered around the cut d^{*}. This requires that non-inertial transport mechanisms (such as electrophoresis or diffusion) be negligible, as they would otherwise yield finite particle deposition rates below d*. One can therefore anticipate resolution problems with either highly charged particles subject to electrical forces, or with very small particles, having substantial diffusivities. Such effects are indeed observed in subsonic impactors, whose size-resolving power deteriorates rapidly due to Brownian diffusion for singly charged particles smaller than 10nm (Fernández de la Mora et al. 1990b). Even more unfavourable effects have been encountered by Rosell-Llompart (1993) with subsonic impactors used to size highly charged (q/e > 1000) electrospray droplets some 0.1 micrometers in diameter. On the other hand, Fernández de la Mora and Schmidt-Ott (1993) find that diffusive effects are relatively small in hypersonic impactors, even for singly charged particles with diameters as small as 2nm. The question now is whether or not this important advantage survives in the case of highly charged ultrafine particles.

2. EXPERIMENTAL

An aerosol is generated electrostatically by the rupture of the jet emitted at the apex of an electrified liquid cone. The scaling laws for the initial droplet size and charge are discussed by Fernández de la Mora and Loscertales (1993) and by Rosell-Llompart (1993). The conductivities of the liquids used are K = 1.26S/m for 1M LiCl in formamide and K = 0.22S/m for a mixture of

NaCl (0.001M) and HCl in water. These droplets are initially approximately monodisperse, with diameters estimated to be in the vicinity of 40nm. They evaporate rapidly, and appear not to undergo Coulombic explosions, as the remaining residue is found to be also monodisperse. The spray is produced inside a closed chamber fed with air, from which it is sampled into the impactor through a narrow tube similarly as in our earlier work with subsonic impactors (Fernández de la Mora et al, 1990c). In some of the experiments, the aerosol is passed first through a mobility filter (cumulative) which excludes the most mobile particles and allows measurement of the mobility of those reaching the impactor. Their mobility distribution is fairly narrow.

The impactor is similar to those described previously by Fernández de la Mora et al (1990a), and Fernández de la Mora and Schmidt-Ott (1993), having a thin plate orifice with a diameter $d_n = 0.37$ mm as the nozzle. It is based on an instrument used by Rosell-Llompart et al. (1991) for the study hypersonic jets of H₂ seeded with heavy molecules. The distance L between nozzle and impaction plate is controlled with a micrometer. The main novelty is that, in order to minimize particle capture due to electrical or diffusive effects, the collector plate is a disk 5.3 mm in diameter, substantially smaller than in earlier work. This collector is connected directly to an electrometer (designed by Dr. H. Burtsher; ETH, Zurich) with a noise level of 0.1fA, with which we measure the flux of charged particles captured. Two types of collectors have been used: one is a smooth brass disk and the other an oiled porous metal frit. The gas (air in all tests) upstream of the nozzle was at room conditions of temperature and pressure. The ratio p_0/p_1 between the pressures in the chambers upstream and downstream the nozzle was 4500 for the experiments with water solutions, and 1160 for those with formamide solutions. The measured flow rate of air was $Q_a = 16.2 \text{ cm}^3/\text{s}$, corresponding to a Reynolds number Re= $4Q_a/(\pi d_n v) = 3735$.

RESULTS

Figure 1a shows three aerodynamic spectra obtained from electrosprays of formamide with the frit disk in the collector. The curves represent the current collected at the impaction plate normalized by its maximum value (the ratio I/I_{max} is interpreted here as the capture efficiency η) as a function of the nozzle to plate distance (in units of the nozzle diameter dn). They have a general shape quite similar to that observed in earlier work with singly charged (mobility classified) monodisperse aerosols. The current reaches approximately a plateau at sufficiently large values of L/dn, and decays at decreasing L through a relatively narrow range of values of L into a minimum, η_{\min} , rising again into a value near 0.2 at L \rightarrow 0. The sharpness of these steps indicates that the aerosol is approximately monodisperse, which is a most remarkable feature in this size range for droplets produced directly by atomization. The value of L/d_n at which $\eta = 1/2$ is simply related to the density ρ_p of the particles and to their diameter d_p , if one assumes that they are spherical (Fernández de la Mora et al. 1990a). The corresponding mean diameters are shown in table 1 together with other characteristics of the spray and the sampled droplets. dmin is the diameter of the impacting particle, calculated under the assumption that ρ_p is that of bulk LiCl (complete evaporation of the droplet into a solid residue), while dmax results from assuming that the droplet density is that of the pure solvent. The difference between the three curves in figure 1a is in the corresponding flow rates Q of liquid pushed through the electrified liquid cone, the smaller flow rates corresponding to the smaller particles (larger values of L/dn at the middle of the step).

In spite of the smallness of the target, the measured values of η_{min} are substantially larger than found earlier for singly charged silver particles 2nm in diameter. This is evidently the result of the high charge on these particles. Table 1 shows also the number N = q/e of elementary charges in each particle, computed as the ratio Z/Z₁ between the measured mobility Z and Z₁, the mobility for a singly charged particle (calculated through the usual mobility-size relations from the diameter inferred from the impactor measurement). Only the values of N corresponding to d_{min} are shown, which yield a lower limit q_{min} for q. The charge corresponding to d_{max} is some 3 times larger. Because the image attraction to the plate is quadratic in N, electrical forces are here between two and three orders of magnitude larger than for singly charged particles. Fernández de la Mora and Schmidt-Ott have speculated that the transport process leading to capture of subcritical particles involves turbulence. This conjecture is further supported by the results of figure 1b for the formamide solution, which show aerodynamic spectra for particles impinging on the smooth collector surface as well as the frit. The two spectra are nearly identical

except for the fact that η_{min} has been reduced practically to zero in the case of the smooth target. This surprising result implies that hypersonic impactors can be freed nearly entirely from undesirable diffusive and image force related particle deposition rates. They appear accordingly as ideally suited for the measurement of nanoparticles produced in electrosprays. The oiled frit was used to avoid particle rebound, thought to be inevitable at impact speeds near 600 m/s. This precaution turns out to be unnecessary, as there is no significant difference at the high L asymptote between the collected current on both types of surfaces. Whether or not the particles bounce after impact, it is evident that they deliver most of their charge to both targets.

Formamide is a relatively involatile liquid, and questions might arise on whether or not the original droplets had dried completely into a salt residue in the measurements just discussed. We have therefore carried out several experiments with NaCl-HCl seeded in water. The corresponding aerodynamic spectra are shown in figure 2, with the characteristics of the spray and the particles summarized in table 1. The effect of the frit is shown in figure 2 to be similar for these particles as in figure 1b. Figure 2a shows that non-inertial deposition mechanisms are negligible at $d_p = 5$ nm. There is little doubt in this case that the droplets must have evaporated nearly completely, as the diameter of the measured residue is substantially smaller than for the formamide solutions, even though the initial size scales as $(Q/K)^{1/3}$ and is considerably larger for the water droplets. It is noteworthy that electrostatic atomization is yielding here fairly monodisperse particles some 5 nm in diameter. The fact that liquid metals emit mostly single metal ions (Gabovich, 1984), makes it probable that even smaller particles may be produced. The remarkable work of Benasayag and Sudraud (1985) imaging by electron microscopy a liquid metal tip, showed nearly a decade ago that this apex emits a jet whose diameter is measured in nanometers.

In conclusion, hypersonic impactors with a small and smooth impaction plate are able to size highly charged nanometer particles produced in electrosprays. The present study has shown this to be the case down to diameters of 5nm, at which it is clear from figure 2a that the instrument's resolution distinguishes quite well between diameters of 5.1, 5.6 and 5.9 nm. We cannot in the present set up analyze smaller particles because the instrument ceases to respond ideally at larger values of L/d_n . However, use of larger pumps or a smaller nozzle diameter would presumably extend its range down to 1 or 2 nm.

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Solution	Q (nl/s)	dmin (nm)	dmax(nm)	Collector	L/dn	N. Charges
Formamide	0.23	10.5	19.2	Frit	2.34	30
Formamide	0.13	9	16.5	Frit	2.73	24
Formamide	0.06	7.5	13.8	Frit	3.27	17
Formamide	~0.06	7.6	13.9	Brass/Frit	3.24	Contra - Street
Water	1.69	5.9	12.8	Brass	4	and an other and
Water	1.25	5.6	12.15	Brass	4.2	-
Water	0.87	5.1	11.1	Brass	4.6	-
Water	1.17	5.6	12.15	Frit	4.2	-





Figure 1a. Spectra obtained from electrosprays of formamide with the frit disk in the collector.

Figure 1b. Spectra obtained from electrosprays of formamide with particles impinging on the smooth collector surface as well as the frit.

Figure 2a. Spectra obtained from electrosprays of NaCL-HCl seeded in water with the frit disk in the collector.

Figure 2b. Spectra obtained from electrosprays of NaCl-HCl seeded in water with particles impinging on the smooth collector surface as well as the frit.

Aerodynamic Lenses for Producing Particle Beams of Controlled Dimensions and Divergence

by

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ABSTRACT

We are developing an instrument for detecting ultrafine particles $(0.01 \text{ to} 0.5 \,\mu\text{m})$ at low pressures (down to 0.1 torr). Our intent is to use this instrument to sample from the pumping lines of semiconductor processing equipment so as to detect particle nucleation from the gas phase. Our apparatus consists of a differentially pumped system for producing a particle beam which is focused through a skimmer into a very low pressure chamber (~10⁻⁵ torr) where the particles become positively charged by secondary electron emission following electron impact. The charged particles are collected in a Faraday cage and detected by a sensitive electrometer. This paper addresses the means by which narrow, non-diverging particle beams are produced in this instrument.

Particle beams are produced by expanding an aerosol through an orifice. Previous investigators have shown that the characteristics of beams produced in this way depend on the nozzle geometry, on particle Stokes number, and on the use of sheath air to confine particles to a specified portion of the flow. We have invented "aerodynamic lenses" which cause particles having small Stokes numbers to move towards the centerline of axisymmetric flows. An aerodynamic lens consists of an axisymmetric reduction or enlargement in the tubular cross section. By using one or more lenses upstream of the nozzle, particles can be moved arbitrarily closely to the centerline without using supplemental sheath air. Because the particles are on the centerline at the entrance to the accelerating nozzle, they remain on axis downstream of the nozzle. Furthermore, because all particles experience the same axial acceleration, particles of a given size are accelerated to the same terminal velocity.

Theoretical and experimental evidence is provided which shows that particle beams produced using aerodynamic lenses upstream of the accelerating nozzle can be significantly smaller in diameter than the accelerating nozzle (e.g., 0.2 mm beams downstream of a 3 mm nozzle). Furthermore, beams that do not diverge significantly over distances of up to 50 cm have been observed.



Figure 2. Schematic diagram illustrating the particle stream contraction factor,

INTRODUCTION

When an aerosol flows through a nozzle, the carrier gas expands rapidly while the suspended particles tend to remain closer to the centerline due to their higher inertia, thereby producing a "particle beam". Previous investigators have studied the characteristics of particle beams that are produced when an aerosol expands through capillaries (Israel and Friedlander, 1967; Estes et al, 1983; Kievit et al, 1990), converging nozzles (Israel and Friedlander, 1967; Dahneke and Flachsbart, 1972; Dahneke and Cheng, 1979; Dahneke et al, 1982), and thin plate orifices (Fernandez de la Mora et al, 1989; Rao et al, 1993). The particle beam characteristics depend on the particle Stokes number, S, defined as:

$$S = \frac{U_n \tau_0}{d}$$

where

 $U_n =$ fluid velocity in the nozzle

 τ_0 = particle relaxation time, based on conditions upstream of the nozzle d_n = diameter of the accelerating nozzle.

Particle beam shape and rate of divergence are highly dependent on the shape of the nozzle and on whether or not sheath air is used to confine particles to a specified portion of the flow. For highly converging nozzles such as thin-plate orifices, particle beams are often found to focus sharply at distances of one to two nozzle diameters downstream of the orifice. Beam diameters as small as 3% of the nozzle diameter were first observed by Fernandez de la Mora et al (1989) using a thin plate orifice with 40% sheath air. Such beams, however, diverge sharply downstream of the focal point, and are unsuitable for application in our instrument. In the case of slowly converging nozzles (capillaries are the limiting case of this type of nozzle), particle beams often cross the axis at relatively large distances, and therefore have small expansion angles. For example, expansion angles as small as 10-4 sr were observed by Israel and Friedlander (1967) using capillaries. However, the beam diameters of such particle beams are often too large to permit the use of small skimmers without losing particles (Estes et al. 1990; Kievit et al. 1990). In our differentially pumped instrument the skimmer separates the intermediate and low pressure chambers; as small as possible so as to minimize pumping requirements. In order to reduce particle beam widths, sheath air can be introduced to confine the aerosol to a narrow region near the centerline of axisymmetric flows (Dahneke and Flachsbart, 1972; Dahneke and Cheng, 1979; Dahneke et al, 1982; Fernandez de la Mora et al, 1989; Rao et al, 1993). For example, Dahneke and Cheng (1979) reduced particle beam diameters by a factor of 10 using 99% sheath air.

We are interested in producing narrow, highly collimated particle beams for particles in the 0.01 to 0.5 μ m diameter range and at aerosol source pressures down to 0.1 torr. To achieve this we have invented the concept of "aerodynamic lenses" which permit particles in a specified size range to be concentrated along the







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Figure 3. Results of numerical calculations for fluid streamlines (a) and particle trajectories (b to e) during flow through system having three aerodynamic lenses. The particle trajectory results apply to particles having Stokes numbers of 0.1, 0.6, 1.5, and 3.0. centerline of the flow upstream of the accelerating nozzle. These lenses provide much the same effect as supplemental sheath air without the disadvantages of the additional gas handling and pumping that are required with sheath air. Beam diameters as small as 0.3 mm (~10% of the nozzle diameter) at downstream distances of 50 cm have been observed, corresponding to an expansion angle of 2.8×10^{-7} sr. Furthermore, transport efficiencies through our apparatus are close to 100%. In this paper the operating principles of aerodynamic lenses are discussed, and numerical and experimental results for particle beam diameters and transport efficiencies are presented.

AERODYNAMIC LENSES: Theory

A generic schematic diagram of our particle-beam-forming apparatus is shown in Figure 1. Particles pass through one or more "aerodynamic lenses" upstream of the accelerating nozzle. These lenses consist of axisymmetric reductions or enlargements in the tubular cross section. As will be demonstrated below, the inward and outward flow accelerations induced by these corrugations cause particles smaller than a given Stokes number to experience asymmetrical radial forces, the net effect of which is to concentrate particles along the centerline of the flow. By using multiple lenses particles can be moved arbitrarily closely to the centerline. The nozzle can also be shaped to move particles closer to the centerline as they are accelerated.

We first consider a lens consisting of a single constriction or expansion, as illustrated in Figure 2. We assume, for simplicity, that the tube radii upstream and downstream of the lens are equal. The particle stream contraction factor, η , is defined as

$$\eta = \frac{r_p(\infty)}{r_0(\infty)}$$

where

- $r_p(\infty)$ = radial location of the particle an infinite axial distance downstream of the lens
- $r_0(\infty)$ = radial location of the flow streamline on which the particle entered the lens.

Note that as long as the flow is laminar, $r_0(\infty)$ is the same upstream and downstream of the lens. Note also that for particles which follow the flow streamlines (i.e., particles with Stokes number = 0), $r_p(\infty) = r_0(\infty)$, so $\eta = 1.0$.

Robinson (1956) showed that in potential flows, particle streamlines tend to converge, leading to local increases in concentration. It follows that for incompressible flows, particles that enter a lens (Figure 1) near the axis will move towards the centerline (i.e., $\eta \leq 1$; Peng Liu, 1993). Peng Liu showed that accumulation along the axis also occurs for compressible, isentropic flows. The theory that predicts movement towards the axis is valid only for sufficiently small particles (i.e., for particles having small Stokes numbers).



Figure 4. Results of numerical calculations for particle beam shapes for lens system exclusing (a to c) and including (d to f) a single prefocusing lens. Calculations for three nozzle designs are shown.



Figure 5. Schematic diagram of experimental apparatus used to measure particle beam shapes.

We have also used numerical flow simulations to investigate the impact of aerodynamic lenses on radial distributions of particles. Unlike the theoretical work above which applies only to small particles near the axis of symmetry, the numerical calculations apply to particles of abribrary size and for all radial locations. Results of these calculations for a convergent lens having inner radius one fourth the tube radius are shown in Figure 3. Fluid streamlines are shown in Figure 3a. Note that under laminar flow conditions, fluid parcels return to their initial radial locations downstream of the lens. Trajectories of particles having Stokes numbers of 0.1, 0.6, 1.5 and 3.0 are shown in Figures 3b. 3c. 3d. and 3e. (Stokes numbers are based on the smallest diameter of the lens and on the highest axial flow speed within the lens). Note that for the three smallest values of Stokes number, particles are moved closer to the center line by each lens element. Particles having S=0.6 move to the axis more quickly than smaller or larger particles. Particles having S=0.1 never cross the center line, while particles having S = 1.5 cross the centerline but eventually converge to the axis. Particles having Stokes number larger than 3.0 impact on the far side of the tube after crossing the centerline. Therefore, these lens systems serve as band pass filters that, in principle, remove all particles larger than some critical size, and move all particles smaller than that size towards the axis. When N lenses are used the particle stream contraction factor is:

 $\eta = \prod_{i=1}^{N} \eta_i$

Since each $\eta_i < 1$, η can be made arbitrarily small by using a large number of lenses in series. Brownian diffusion and turbulent fluctuations will, in practice, limit the extent to which particles can be concentrated along the axis. Our analysis neglects these effects.

The effect of aerodynamic lenses and of the shape of the accelerating nozzle on downstream particle beam characteristics have also been investigated numerically. Results of these calculations for 0.1 μ m DOS droplets are shown in Figure 4 for three different nozzle designs, both with and without a single prefocusing lens. When included, the prefocusing lens was located 60 mm upstream of the nozzle, and consisted of a 10 mm long, 4 mm diameter capillary. The nozzles each consist of short (10 mm) capillaries located immediately upstream of a 2.9 mm thin-plate orifice. Capillary diameters of 2.9, 5.9 and 7.9 mm were used. Note that the nozzle equipped with the 5.9 mm capillary produces narrower beams than either the larger or smaller capillaries. The larger capillary produces insufficient flow convergence to have much effect; in this case the performance of the orifice approaches that of a thin-plate orifice. The smaller diameter capillary is of the same diameter as the orifice, and therefore this nozzle produces beams characteristic of a capillary. Note also that in all cases investigated beams become more highly collimated when prefocusing is used.

In the following section experimental measurements of particle beam shapes are presented and compared with theoretical predictions. We also show that





Figure 6. Comparison of calculated and experimentally determined beam shapes for a beam formed from 0.037 um DOS particles without prefocusing. The open circles mark the measured 90% contour (i.e., 90% of the particles are located at radial distances less than or equal to these values), and the dashed line represents the calculated 86% contour (which should be very close to the 90% profile). The faint dotted lines correspond to individual particle trajectories.



Figure 7. Beam diameters 75 mm downstream of a 2.9 mm orifice; 90% of the measured particle current falls within the indicated diameter. Data are shown both for inlet tubes equipped with (solid circles) and without (open circles) prefocusing lenses. The three figures apply to three different nozzle geometries.

because we are able to produce narrow, highly collimated beams, particles are transported with near 100% efficiency through our instrument.

PARTICLE BEAM SHAPES: Experimental Results

Particle beam shapes are measured using the apparatus shown in Figure 5. Monodisperse, singly charged particles produced with a differential mobility analyzer (DMA; Liu and Pui, 1974) are expanded through a pressure reducing orifice to the desired sampling pressure (0.1 to 10 torr). The low-pressure aerosol then flows through an inlet tube towards the accelerating nozzle. A sensitive electrometer is used to measure the current delivered by the charged particles to a Faraday cup detector located downstream of the nozzle. Beam diameters are determined by measuring the decrease in current as a knife edge is moved across the particle beam by a micrometer. We have done measurements both with and without aerodynamic lenses in the inlet tube.

Results of one set of measurements of particle beam shape are illustrated in Figure 6. Note that in this case no prefocusing lenses or other were used to center the aerosol before it was accelerated through the thin-plate orifice. The particle beam boundaries that are shown by the open circles contain 90% of the particles. Note that under these conditions the particle beam diameter was about 10% of the nozzle diameter at a distance of 15 mm (~5 nozzle diameters) downstream. Results of calculated beam shapes for this experiment are also shown in Figure 6. Note that our numerical model, which assumes isentropic compressible flow, and which does not include the effect of shocks, is in reasonable agreement with measurements. While sytematic comparisons between theory and experiment for these nozzle geometries and prefocusing lens configurations are not yet complete, these results are qualitatively consistent with the numerical results shown in Figure 4.

Results of experiments to examine the effect of aerodynamic lenses and nozzle geometry are shown in Figure 7. In this case all measurements of beam diameter were made 75 mm downstream of the nozzle. Reported beam diameters contain 90% of the measured particle current. The data shown with solid circles were obtained using a single aerodynamic lens upstream of the accelerating nozzle; no prefocusing was used for the data shown with open circles. Figures 7a, 7b and 7c apply to different nozzle geometries. For Figure 7a the nozzle consisted of a 10 mm long capillary tube that was equal in diameter to the orifice $(d_t=d_n; \text{ see Figure 1})$. The nozzle used for Figure 7b consisted of a 10 mm long, 5.9 mm diameter capillary tube attached to the upstream side of the 2.9 mm nozzle, while a 7.9 mm diameter capillary tube of the same length was used for Figure 7c. In all cases the diameter of the inlet tube, di, was 10 mm. Note that including the 4 mm prefocusing lens led to narrower particle beams in all cases. The narrowest beams were obtained when the prefocusing lens was used in conjunction with the 5.9 mm diameter capillary tube upstream of the nozzle orifice (Figure 7b). The larger capillary tube (7c) was not effective in constricting the flow before it entered the orifice, so did little to center the aerosol before it entered the orifice. Because the smaller capillary (7a) is the same size as the orifice, the entire nozzle consisted of a single capillary. Previous work has shown that capillaries have no focusing effect. Therefore, of the



Figure 8. Schematic diagram of apparatus used for measuring particle transport efficiencies.

three sizes investigated the intermediate-sized nozzle produced the narrowest beams.

PARTICLE TRANSPORT EFFICIENCIES: Experimental Results

In order to obtain quantitative information on particle concentrations it is necessary to know the efficiencies with which particles are transported from the low pressure source region through the instrument to the Faraday cut detector. A schematic diagram of an apparatus used for measuring particle transport efficiencies through our apparatus is shown in Figure 8. Monodisperse, singly charged DOS particles in the $0.02 - 0.25 \,\mu$ m diameter range were produced with a DMA. This monodisperse aerosol flow is split immediately downstream of the DMA. A portion of the flow (Q_{ref}) is directed to an atmospheric -pressure electrometer which measures the electric current associated with the particles immediately downstream of the DMA (I_{ref}). The remainder of the aerosol ($Q_{chamber}$) expands through a critical orifice into the aerosol source chamber which simulates the sampling region downstream of the semiconductor processing tool. this orifice reduces the pressure from one atmosphere to a value in the range 0.1 to 5 torr.

Particles in the source chamber are drawn through the differentially pumped particle beam lens-skimmer assemble. The purpose of the skimmer is to provide an additional step of pressure reduction. The particle detection scheme that we are using (electron impact charging downstream of the skimmer followed by measurement of current delivered by the charged particles to a sensitive electrometer) requires a pressure in the range of 10⁻⁵ torr for satisfactory performance of the electron gun used to charge particles. The pressure in this chamber is maintained using an 8" Turbomolecular pump. Most of the gas is removed by a mechanical pump that is connected to the system between the nozzle and skimmer. The particles are focused through the skimmer, as illustrated in Figure 9, and are collected by the Faraday cup (Figure 8). The efficiency of particle transport through the pressure reducing orifice, the lens-nozzle assembly, and the skimmer is then:

Transport Efficiency = $\frac{I_{beam}}{Q_{chamber}} \cdot \frac{Q_{ref}}{I_{ref}}$

where I_{beam} is the current delivered to the Faraday cup in the low pressure chamber.

Results of transport efficiency measurements for our apparatus are shown in Figure 10a and 10b. For these measurements the aerosol source chamber was maintained at 1.47 torr, and the nozzle tube (d_t) and nozzle orifice (d_n) diameters were maintained at 6 and 3 mm, respectively. No prefocusing was used. The data in Figure 10a show the dependence of transport efficiency on the nozzle orifice-to-skimmer distance (H) for a skimmer size of 0.75 mm. Note that transport efficiencies are higher for H=15 and 24 mm than for H=6 mm. Note also that transport efficiencies for H=15 and H=24 mm depend systematically on particle size, but that for the range of particles investigated, transport efficiencies ranged from 50% to 90%. The data in Figure 10b were obtained using similar experimental



Figure 9. Conceptual illustration of particle beam formation downstream of the nozzle. Note that the gas mostly impacts on the skimmer plate and is removed by the intermediate pressure pump, while particles that have sufficient inertia are aerodynamically focused into a narrow, highly collimated beam that is transported with high efficiency through the skimmer.
conditions to those for Figure 10a, except that a larger skimmer (1.75 mm) was used. Note that in this case, transport efficiencies were close to 90% for the entire range of particle sizes investigated.

These measurements showed that for a certain particle size range it is possible to have near 100% transmission efficiencies even when the diameter of the skimmer is only 25% of the nozzle diameter. This indicated that particles are concentrated near the axis as they pass through the nozzle, as illustrated in Figure 9. From Figure 9 it is also clear why the nozzle-to-skimmer distance H can have such a large effect on sampling efficiencies: if the skimmer is located to close to the nozzle where the beam has not yet converged, or too far from the nozzle where the beam has begun to diverge, particles will be intersected by the edge of the skimmer and transport efficiencies will be reduced.

Prefocusing was not included for the measurements that are shown in Figure 10, and we have not yet completed experiments that use prefocusing lenses. However, based on the results that are discussed above we anticipate that transport efficiencies will be less dependent on nozzle-to-skimmer distance when prefocusing is used. We also expect that transport efficiencies will be closer to 100% over a broader range of sizes.

CONCLUSIONS

We are developing a particle beam device for detecting ultrafine particles (0.01 to 0.5 μ m) in low pressure (down to 0.1 torr) systems. A differentially pumped apparatus is used to draw aerosol through a particle-beam forming assembly into an intermediate pressure chamber where most of the gas is removed. Particles are focused through a skimmer into a low pressure chamber (~10⁻⁵ torr) where they pass through an electron beam (typical electron energy~250eV). Following electron impact particles become positively charged by secondary electron emission. In order to achieve high transport efficiencies as well as high charging efficiencies, it is essential that our particle beams are highly collimated and as narrow as possible. We have invented "aerodynamic lenses" which permit us to produce such particle beams. With these lenses, collimated particle beams can be produced for all particles smaller than a critical Stokes number.

An aerodynamic lens consists of an axisymmetric constriction or expansion in a tubular flow. The radial inward and outward fluid motion that occurs as a result of such flow disturbances causes radial forces on particles that lead to net movement towards the axis provided that particle Stokes numbers are below some critical value, S_c . Particles having Stokes numbers exceeding S_c impact on the tube wall. By using multiple lenses all particles having Stokes numbers smaller than S_c eventually are transported to the center line, while particles larger than this are removed. If this approach is used to center the particles before they are accelerated through the beam-forming nozzle, particles remain on axis resulting in narrow, highly collimated beams. Furthermore, because all particles experience the same acceleration, the terminal velocities for particles of a given size are all equal. Uniformity of particle velocities is desirable if the apparatus is to be used for measuring particle size distributions by electrostatic deflection.



Figure 10. Results of transport efficiency measurements. Experiments were done using monodisperse DOS particles.

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Nonsteady-State Filtration of Submicron Aerosols in Fibrous Filters

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Abstract

The rational design of a filtration process should be based on reliable predictions of the dependence on the effluent concentration and of the pressure drop on the time for a given set of operating conditions i.e. particle concentration and size, filter packing density, size of filter element, velocity of the gas and others. The pattern of filling of the internal space of the porous structure of filters is described qualitatively. Deterministic and stochastic models of dendrite growth, after nuclei have been deposited on the surface of fibers are analyzed. Local porosity changes in time and its influence on pressure drop and deposition efficiency have been determined with fractal theory.

Introduction

Filtration in a structure of fibrous filters is a process used extensively to remove suspended particulate matter from the gas stream. As the gas-solid suspension flows through a packed bed of fibers, a substantial number of the suspended particles are deposited on the fiber surface, the end result being the separation of the suspended matter from the gas medium. The particles penetrate considerably into the porous medium and deposit at various depths. The rational design of a filtration process should be based on a reliable prediction of the dependence of the effluent concentration and of the pressure drop on the time for a given set of operating conditions, since both the effluent concentration and pressure drop change during the operation of the filter. Macroscopic behaviour of a bed grain filter is described by Payatakes et al. (1977).

Consider now, a dilute suspension of submicron particles in a gas. The suspension flows through a layer of a fibrous filter of thickness L and porosity ε , (Fig. 1) with a constant superficial velocity v_0 .



Fig.1. Suspension flow through filter layer.

The concentration of particles in suspension is characterized by the volume fraction c (volume of suspended matter per unit suspension volume). Filtration takes place throughout the depth of the bed.

A particle volume balance on a differential section of the filter layer along direction 1, gives:

$$\frac{\partial (w+\varepsilon \cdot c)}{\partial t}\Big|_{l} + v_{0}\frac{\partial c}{\partial l}\Big|_{t} = 0$$
 (1)

where w is the volume of deposited matter per unit bed volume.

The porosity ε of the filter medium will change as particles deposit. If ε_0 is the porosity of the clean filter, we have:

$$\varepsilon - \varepsilon_0 - \frac{w}{1 - \varepsilon_d} \tag{2}$$

where ε_d is the porosity of deposited matter. In the further way is the further way is a second In the further analysis the attention will be focused on the dependence of ε_{1} on the time. Equation 1 should be completed with the filtration equation describing the rate of particle deposition in terms of w and c. The filtration equation has the form:

$$-\frac{\partial c}{\partial l}\Big|_{t} -\lambda \cdot c(l,t) \tag{3}$$

From the physical point of view, λ can be interpreted as the number fraction of particles retained per unit length of filter layer. Generally λ is dependent of c, which is equivalent to assuming that the probability of each suspended particle to be captured is dependent on the presence of deposited particles with formation of internal porous structure of porosity e.

The pressure gradient at any position in the layer depends on the amount, nature and structure of the deposited matter. Taking the phenomenological approach one can write:

$$\frac{\partial p}{\partial l}\Big|_{t} - \frac{dp}{dl}\Big|_{w=0} \cdot f(w, \varepsilon_{d})$$
(4)

where $(dp/dl)|_{w=0}$ is the pressure gradient along the clean filter layer, and $f(w, \varepsilon_d)$ is a function of w and of the recent structure of deposit inside the filter.

One can see from Eqs. (3) and (4) that the key points for exact analysis of filter behaviour are the dynamics of deposit structure growth and its geometrical form.

Dynamics of deposit structure growth.

When an aerosol of fine solid particles flows through a fibrous filter, particles deposit on fibers and form chainlike agglomerates known as dendrites. These dendritic structures grow relatively unhindered for an initial period of time, but eventually they begin to interfere with each other's growth and intermesh (Fig.2).



Fig.2. SEM pictures of early stages of dendrite growth and initiation of intermeshing.

This pattern of deposition has profound effects on the filtration efficiency and pressure drop ($\lambda(t)$ and f(w, ε_i) respectively), both of which increase rapidly with time. Therefore, rational design, optimization, operation troubleshooting and innovation require intimate understanding and accurate analysis of the dendritic deposition process. A theoretical model of dendritic deposition for the period during which dendrites do not intermesh was developed by Pavatakes (1977) and extended to the cases of convective Brownian diffusion and electrostatic interaction of submicron particles for wide range of Knudsen numbers by Payatakes and Gradon (1980), Gradon and Payatakes (1982), and Gradon (1980). Deposition is analyzed for a single fiber element. It was found that the deposition pattern is strongly sensitive to the flow structure around fibers. Recent models of air flow around an array of cylinders rather poorly describe the phenomenon. A New model of gas flow around cylinders developed by Podgórski (1993) is the best approximation of the flow structure. The approximate fluid flow pattern around a single fiber at low and intermediate values of Reynolds numbers can be obtained based on the Oseen's equation of motion. Using methods of complex disturbance velocity, the solution is split into harmonic and non-harmonic parts and they can be expressed in the form of Fourier-Bessel series. The coefficient in the solution comes from the boundary conditions. The solution obtained takes into account effects of fluid inertia and correctly predicts the existence of standing, closed eddies at the rear of the fiber for Re>5. Because of its analytical form and simplicity the method may be useful for analysis of dendrite growth for more realistic structure. Fig. 3 shows an example of streamlines around single and double fibers.

According to the definition of idealized structure a dendrite is a set of integers $\{M_k(t,\Theta), k=1,2,...\}$ where M_k is the number of particles in the k-th layer of dendrites (Fig.4), where t is the time since the nucleus is deposited at site Θ on the surface of the fiber. Thickness of the layer is defined by the aerosol particle diameter. Stochastic simulation is a natural way of describing of dendrite growth, but it is not in essence involved in the analysis of the mechanisms of the process and the influence of the particular parameters on the phenomenon. At the beginning the deterministic idealized model will be described. According



Fig.3. Gas flow structure around single fiber and pair of fibers.



Fig.4. Idealization rules for dendrites growth analysis.

to this idealization, dendrites are composed of monosized particles that belong to distinct layers, and the object of the model is to express the expected number of particles in the k-th layer of dendrite m_k as a function of dendrite age t, and the angular coordinate of the nucleus position Θ .

For a given dendrite:

$$\frac{dm_k}{dt} - R_{k-1,k}^{(s)} + R_{k,k}^{(s)} + R_{k+1,k}^{(s)} \qquad k-1,2,3,\dots$$
(5)

where $R^{(9)}_{i,k}$ is the rate of increase of m_k by deposition on particles occupying the i-th layer due to the flow component in the s, direction (s= Θ , s=r for a polar coordinate system for example). The maximum number of particles in a given layer that can be attached to one and the same particle in an adjacent layer is limited by the so called coordination number which is the result of the packing of spheres in a space.

Values of R, can be calculated from deterministic equations describing particle motion in a field around the fiber and the local particle of a dendrite. In this particular case the convective diffusion equation with an additional drift of the particle due to different electric forces (Coulomb, image, dipole) can be used. Solution of equation (5) with the initial condition which defines the position of nuclei gives us the dynamics of dendrite growth and its local structure i.e. number of particles or total surface of dendrite and dendrite distribution around a fiber; Payatakes and Gradoń (1980), Gradoń (1980), Gradoń and Payatakes (1982).

The shape of a dendrite, as well as dendrite distribution, depend on the fiber Reynolds number, Peclet number, Knudsen number and electric force. The picture of dendrites changes from slender and long dendrites to short compact shapes (with many local branches in reality). The model described above for an assumed set of parameters can predict the final shape of a dendrite.

A realistic shape of a dendrite is obtained via simulation and visualization of the capture of particles on the fiber and on the already deposited particles. A personal computer program, FiFi, has been developed, which makes a two-dimensional simulation in real time of the behaviour of particles in an air flow around a fiber in an electric field. This simulation includes the motion of particles, the capturing mechanism and the formation of dendrites on the fiber, Lastow (1992), Lastow and Gradon (1993). FiFi can be used to simulate the influence of dendrites and large numbers of independent parameters on the filtration efficiency of a single fiber. It is also very useful to visualize how the particle dynamics depend on various parameters. There are two kinds of transport mechanisms: one deterministic and one stochastic. These mechanisms have two different time aspects. Two different time intervals are used: the relaxation time $\tau (= \varrho d_p^2 C_c/(18\mu))$, where C_c is Cunningham correction factor and Δt which is fraction of τ . At the position \mathbf{r}_{ii} , the particle has the velocity V_{ij} and an acceleration $a_{ij} = F_{ij}/m$, where F_{ij} is the force vector acting on a particle of mass m. The deterministic step s_{ii} occurs every Δt and the stochastic step s_{ii} , every τ . The stochastic step is the distance the particle moves due to diffusion. The deterministic step is calculated as follows:

$$S_{i+1,j} - \int_{\Delta t} V_{i,j} + \frac{1}{2} \Delta V_{i,j} dt$$

(6)

where:

$$\Delta V_{i,j} - \int_{\Delta t} \frac{F_{ij}}{m} dt$$

And the stochastic step is:

$$s_s = \sqrt{2D\tau \cdot n}$$

where the particle diffusion coefficient $D = kTC_c/(3\pi\mu d_p)$ and **n** is the unit vector of the stochastic jump. The direction **n** is randomized with an assumed probability distribution. The new particle position after τ is given by:

$$\boldsymbol{r}_{i+k,j+k} - \boldsymbol{r}_{i,j} + \sum_{l=1}^{i+k} \left(\int_{\Delta t} \boldsymbol{V}_{i,j} + \frac{1}{m} \int_{\Delta t} \boldsymbol{F}\left(\boldsymbol{r}_{i,j}, \boldsymbol{V}_{i,j}\right) dt^2 \right) + \sqrt{2D\tau} \cdot \boldsymbol{n}$$
(9)

(7)

(8)

The movement of the particle and the capturing mechanism are implemented graphically (Fig.5).





The dynamics of dendrite growth and the final shape of the dendrite can be observed from the computer screen.

Another approach for dendrite growth analysis is the Monte Carlo simulation, which is especially useful for diffusion-controlled cluster growth. Association of results of that method with the determination of fractal Hausdorff-Besicovitch dimensionality, is an object of many papers published recently, Meakin (1980), Nagatami (1980), Witten and Sander (1983) and others.

An extension of the Monte Carlo simulation was used and extended to the case of the existence of deterministic drift $\mathbf{\tilde{u}}$ of the particles resulting from the convection of flowing gas

and electrostatic interactions for example. In such simulations particles follow lattice randomwalk trajectories and an underlying lattice is used to inform the random walker how long the next step in the walk may be. The step length is strictly incorporated with the value of the Peclet number which is related to the diffusion of the particles (random) and the deterministic drift (Pe=ud/D where d is a linear dimension). If P(x,k) is the probability that the walk reaches site x at the k-th step, the continuum version of the process is described by equation:

$$\frac{\partial P}{\partial t} + \overline{\nu} \nabla P - D \nabla^2 P \tag{10}$$

The normal growth velocity of a cluster V_n is defined as:

$$V_{n} - D \cdot n \cdot \nabla P \tag{11}$$

Stability analysis of the dendrite growth governed by convective diffusion was done for the solidification process, Müller-Krumbhaar and Langer (1981), Langer (1980), and was applied for the freezing-out separation process, Gradoń and Orlicki (1984, 1985).

Stability and universality of the clustering for diffusion-controlled growth was done by Witten and Sander (1983). Scale invariance for convective diffusion and determination of the scale factors which contain the information about the Hausdorff dimension of the object is the key point of the analysis. In our case it was done for the aggregation process for a two-dimensional motion of a particle in a square-lattice field with a small drift on it (Fig.6).



Fig.6. The model used to simulate the effect of drift $\bar{\mathbf{u}}$ and the "black hole" presence on DLA.

We start with a single "nucleus" particle at the center of the lattice. Some part of the lattice which corresponds to the space taken by the fiber is treated as a "black hole". Such situation focuses us on the growth of the particular branch of the dendrite. A second particle is added a long distance from the origin, r_{max} , and can come from the space defined by d_{max} , and

undergoes a random walk with drift on the lattice until it reaches a site adjacent to the seed and becomes part of the growing cluster. If the particle reaches a position far from the nucleus, it disappears. Then the particle is released. The density-density correlation of growing dendrites has a power function with exponent D_{H} -2, where D_{H} is the Hausdorff (fractal) dimension of the process.

Results and discussion.

Dendritic structure growth for all three methods described above were calculated for submicron particles characterized by the particle diffusion coefficient and convective effect measured with vector $\mathbf{\tilde{u}}$. The first deterministic method gives idealized dendrites, but also gives an explicit relation between the influence of particular parameters and dendrite structure. FiFi methods give a realistic shape of the dendrites, but that shape can be seen post factum. The simulation described in the third method is especially useful for analysis of stability of dendrite growth and the prediction how the structure fills the Euclidean space; in the estimated vector. All methods are in good agreement with the prediction of the slenderness (branching) of dendrites depending on the values of the parameters ($\mathbf{D}, \mathbf{\tilde{u}}$). For the deterministic method the coordination number was assumed to be 3. Two other methods predict an average value of approximately 2.3.

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CHARACTERIZATION OF NANOMETER PARTICLES

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Small particles are gaining increasing importance in a number of very different fields. These include for example clean room technology: namely as the dimensions of semiconductor devices decrease, the size of particles which may cause problems is reduced accordingly. Other interesting fields are particle production in combustion processes or manufacturing of nanophase materials via the aerosol phase.

Adequate methods for particle detection and characterization are required no matter whether the aim is to produce particles with the desired properties or avoid particle production in emissions from combustion, or to keep delicate chips clean of depositions. These tools may be off-line analytical methods, but can often be sensors operating continuously to monitor or control particle processes.

In the following some methods will be described which we feel are very powerful and/or can be realized without excessive auxiliary equipment yet give relevant information on shape, density and surface properties of the particles.

TEM and STM analysis

In most investigations, information on size, shape, and structure of particles is obtained by the transmission electron microscope (TEM). TEM is used to study primary particles and agglomerates. In fact, studies concerning the fractal properties of agglomerates are mostly based on TEM analysis. High resolution TEM yields information at the atomic level. Figure 1 shows an image of a particle, found in the exhaust of a combustion engine, operated with leaded fuel. The exhaust gas was annealed to a temperature of 275°C (Steiner et. al.,1992). Before annealing the lead is in islands embedded in carbon particles, after annealing lead and carbon are segregated. The high resolution allows to detect the almost perfect monocrystalline structure of the particle. EDX-analysis shows that the crystal consists of Pb and Br, the Br being added to the fuel as lead scavenger. Such images yield much information, but they are always a two dimensional projection. Some information on the third dimension can be obtained with a shadowing technique which also allows to improve the poor contrast obtained with light elements, for example carbon. A very thin metal film (Ta/W) is evaporated on the sample at an angle of 45°. The 'shadow' of the particle on the sample holder then shows its third dimension (figure 2).

Another way to obtain a three-dimensional image of the particles is to use a scanning tunneling microscope (STM). The STM is known to be a very powerful tool for the investigation of

interfaces and surfaces. For STM analysis, we precipitated the particles on a highly oriented pyrolytic graphite (HOPG) substrate. HOPG is very convenient because it provides a flat surface if cleaved.



Fig. 1: High resolution TEM image of lead particle, sampled in the exhaust of a combustion engine

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Fig. 2: TEM image of combustion particles after coating the sample with a Ta/W film by evaporation at 45 °.



Figure 3 shows an STM image of an Ag particle, produced by an evaporation/condensation aerosol generator and size selected by a differential mobility analyzer (DMA, Reischl, 1991). For comparison TEM samples have also been taken in parallel to the STM sampling. From the TEM analysis the particle density on the substrate is estimated to be about 100 μ m⁻³. This means that on the scanning area in figure 3 about 30 particles have to be expected. However, only one is actually found. Most probably this is due to movement of particles by the STM tip

which sweeps the scanning area clean. Traces of moved particles found on some images corroborate this hypothesis. The particle in figure 4 has been dragged over a step in the substrate, leaving a trace before it adheres stabily (Schleicher et al., 1993a). Once a particle is in a stable position, zooming makes atomic corrugation clearly visible (figure 5).



Fig. 4: Silver particle pushed across a step in the HOPG substrate, leaving a visible trace



Fig. 5: Small area scan of the particle in figure 3, showing atomic resolution.

The size found by the STM analysis is in good agreement with the setting of the DMA. However, the particles appear completely flat. This is not only observed for Ag but also for C particles. Both have a height of only about 10% of their width. The reason of the flattening is not yet clear. Possible explanations are that the particles are flattened by interaction with the tip, that the scaling of the z-axis is incorrect due to a poor electrical contact between particle and substrate, or that a selective imaging of flat particles occurs, because only these adhere enough so that they are not moved away by the tip.

These examples show that STM imaging is an interesting way to visualize particles in the nanometer range, even more information can eventually be obtained by using an atomic force

microscope. However, some problems concerning the interpretation of such images remain to be solved.

The particle imaging techniques shown above give quite detailed information on the particles, however, they require particle sampling on a substrate. This means the particles are measured neither in situ nor on line or continuously. Additionally sampling the particles on a substrate may cause artifacts. For many applications a fast continuous measurement is required. In the following such monitoring techniques will be presented.

In situ determination of size and density by mobility analysis and low pressure impaction

Size and mass are important parameters for the characterization of particles. Measurement of mass versus size yields information on the particle structure and allows one to determine a fractal-like dimension from the relation

(1)

This can be achieved by the combination of mobility analysis and low pressure impaction.

Particles are first selected according to their mobility diameter in a differential mobility analyzer (DMA, Reischl, 1991). The monodisperse aerosol then enters a low pressure impactor, operated in the subsonic range as described by Fernandez de la Mora et al. (1990). The cutoff diameter of the impactor is scanned by the impactor pressure. Thus mobility diameter and aerodynamic diameter of the particles are measured, which allows one to also determine the mass. The system consisting of DMA and impactor is controlled by a computer. This achieves automatic measurement of a set of curves as shown in figure 6. For each setting of the DMA (= each selected mobility diameter) the impactor pressure is scanned over the range where the impaction efficiency changes from zero to one. The aerodynamic diameter is determined from the pressure at which the impaction efficiency is 50%.

The impactor is calibrated with DOS (dioctyl sebacate) particles. DOS is a low volatile oil. As these particles are liquid, they are spherical and have a well defined density.

Metal particles (Ag, Co, Pd) are produced by evaporating from a heated wire (evaporation/condensation type aerosol generator). The densities obtained in the impactor are generally all too low by a factor of ≈5 compared to bulk densities. Hering and Stolzenburg (1992) have observed this phenomenon as well. The relative densities, however, are correct. The reason for this discrepancy occurring with ultrafine particles is not yet understood.

The particles have been analyzed immediately after production (primary particles) and after remaining in a coagulation chamber for about 4 min. Table I shows the fractallike dimension d_f , obtained for agglomerated and non agglomerated particles using eq. (1). Schmidt-Ott et al. (1990) discuss the restrictions for the use of the mobility diameter to determine d_f .



Fig. 6: Set of impaction curves of small Pd particles, the impaction efficiency is plotted vs. the upstream impactor pressure.

	d _f , primary particles	d _f , agglomerates
DOS	3	
Ag	2.95	2.75
Pd	2.95	2.75
Co	2.75	2.3

Table I: fractallike dimensions, obtained for DOS, Ag, Co, and Pd

As expected, the non agglomerated particles exhibit $d_f \cong 3$, with the exception of Co particles. The lower d_f found for Co particles indicates that agglomeration occurs immediately after production. The values of d_f found for agglomerates indicates a mixed monomer-cluster and cluster-cluster agglomeration. The different behavior of Co may be due to magnetism enhancing agglomeration. For a more detailed description see Schleicher et al. (1993b).

Particle analysis by photoelectric charging

In photoelectric charging of particles (PCP), the gas containing the particles is irradiated with ultraviolet light. The energy hy of the photons has to be below the ionization threshold of the gas molecules, but above the photoelectric threshold hyo of the particle. The gas molecules remain then electrically neutral, whereas the particle may absorb a photon and emit a photoelectron. The photoelectron emission depends on the optical absorption α of the light and especially on the state of the particle surface as hv_0 as well as the probability k of escape of the electron over the surface barrier potentials depends critically on the nature and amount of adsorbates at the surface. However, whether or not the particle remains with a positive charge after photoelectron emission hinges on whether or not the photoelectron diffuses back to it. It turns out that in air at barometric pressure and ambient temperature, particles with diameter $D < 1 \mu m$, that is nanometer particles, are charged with high efficiency. In this case, the photoelectron diffuses to the walls or electrodes of the photoemission chamber leaving behind a positively charged particle. To detect PCP, all particles are precipitated in a filter. The electric current i flowing from the filter to ground potential yields the total photoelectric charge generated per sec. If the incident photon current density jhy is small, double charging of particles is unlikely and we have

$$i = i_{h\nu} N \cdot F \cdot \alpha \cdot k (h\nu - h\nu_0)^m$$

(2)

where F is the surface area of the particles, N the number of particles, and m an empirical constant (Burtscher et al., 1982).





The principle of PCP is shown in Fig. 7. The gas carrying the particles enters a quartz tube in which it is exposed to the light emitted from an UV-lamp. The positively charged particles are collected in the filter and i in eq.(2) is measured with the current amplifier.

The application of PCP to combustion particles is described in detail by Burtscher (1992). Here the detection and analysis of ultrafine particles in emissions from volcanoes will be used to show some features of PCP. High concentrations of nanometer sized particles are produced by nucleation of volatiles, degassing from the magma when the volcanic gases cool down.

Particles are measured at the rim of the volcano. As the dilution of the sampled gas depends for instance on wind direction and wind speed the measurement of the total photoelectric charge alone is not meaningful. Therefore the charge which the particles acquire by attachment of ions from an electrical corona discharge, is determined in a parallel measurement. The ratio of photoelectric charge and charge by ion attachment, called photoelectric activity ε , depends only on particle material properties and no longer on concentration, dilution or particle size. A continuous measurement of ε at Mt. Etna in summer 1991 and several shorter measurements at Mt.Etna and other volcanoes clearly show a relation between ε and the volcanic activity (Ammann et al., 1990, Ammann et al., 1992a).



Fig.8 Photoelectric activity (solid line) and furnace temperature (dashed line) in a lava degassing experiment as function of time

Lava degassing experiments in the laboratory and measurement of photoemission from a variety of salts and salt mixtures, expected in volcanic emissions, indicate that ε is a measure for monovalent copper occurring as CuCl in the particles (Amman et al., 1992b). As CuCl is relatively volatile, it degasses at an early stage from the magma. Its presence in the particles is

therefore an indicator of fresh magma (Ammann et al. 1993). The result of a degassing experiment is shown in figure 8. A lava sample is heated in a tube furnace in an air flow. When the gas cools, particles are produced by homogeneous nucleation from degassing material. ε and furnace temperature T are plotted versus time. ε is high only in a small range of temperatures . At higher temperatures it decreases drastically. Figure 9 shows XPS spectra of the Cu 2p levels from samples taken during the period of high ε and, for comparison, of monovalent and divalent copper, giving a clear evidence for the presence of monovalent copper in the particles. The presence of CuCl indicates delivery of fresh magma to the crater region. The simple PCP measurement therefore yields interesting information on magmatic processes, which may be used to monitor volcanic activity and which is potentially useful for forecasting volcanic events. As the instrument is very simple, portable devices, which can be operated even in the hostile environment of an active volcano are possible. For a more detailed description of these experiments see Amman et al. (1992b and 1993).





c) pure CuCl particles after exposure to air (divalent copper on the surface)

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Application of Photon Correlation Techniques to Ultrafine Particle Analysis

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Abstract

The theory of dynamic light scattering on aerosol particles at rest and in uniform motion is briefly discussed. The problem of data inversion for polydispersed particles is addressed. Experimental results for particle size measurements in the nanosize range are presented.

1 Introduction

In contrast to most other optical methods photon correlation spectroscopy exploits the time dependent properties of the scattered light. The time dependence of the scattered light (we do not deal here with the statistical nature of the light emitting process itself) is governed by the dynamic properties of the scattering medium. The interrelation between these material properties and the scattered light is given by the dynamic light scattering theory. Photon correlation spectroscopy is a technique to measure this dynamic properties in the time domain. The same information is available in the frequency domain and can be extracted from line shape measurements for example.

The theoretical analyses of the relation between the statistical properties of signal fluctuations of light detectors and the statistical properties of light fields started in the late sixties and early seventies and photon correlation spectroscopy emerged quickly as a powerful tool to analyse dynamic material properties experimentally. In effect such properties as the diffusion coefficient or temperature conductivity were among the first properties determined by this technique. But also Brownian motion came quickly into the view of theoreticians as well as experimentalists as an interesting field for this new technique. This is the point, were particle analyses came into play. It is well known, that particle size plays an important role in Brownian motion. It is obvious that larger particles are not as easily pushed around by molecules as smaller ones. The quantitative relation between particle size and particle diffusion coefficient, as a measure of the Brownian random walk, was given by Einstein. It is this relation and its refinements which makes it possible that information on the particles size of Brownian particles can be extracted from dynamic light scattering experiments.

2 Physical background

It may be instructive to summarize briefly conventional light scattering techniques for particle size determination. If the particle size is not small compared to the wavelength of the scattered light, the angular distribution and the depolarization of the scattered light strongly depend on



Sizeparameter x = 0.1 Sizeparameter x = 1.0



Sizeparameter x = 10

Sizeparameter x = 100

0

10

315

Fig. 1. Angular distribution of scattered light as function of size parameter.

the particle size or more precisely on the size parameter, which is for spherical particles the ratio of particle diameter to wavelength. In most cases one can assume that the particles scatter the light independently of each other and multiple scattering is negligible. In this case the total scattered intensity is a function of particle size and particle number concentration. The size can be determined from the angular distribution of the scattered light or from depolarization measurements. The number concentration can then be deduced from the intensity of the scattered light.

If however the particles are small, if their size is only a fraction of the wavelength, the angular distribution of the scattered light is simply that of a dipole radiation and independent of the particle size, Fig. 1. Only for absorbing particles a measurement of the scattered and the absorbed light gives the opportunity to separate the contributions from particle number and from particle size from each other. The absorption can be determined by measuring the fraction of transmitted light e.g. Additional problems appear from scattering from the gas molecules, which have the same dipole characteristic as small particles.

In the case of photon correlation spectroscopy not the intensity of the scattered light but the time dependent fluctuation of the intensity of the scattered light is exploited for particle size determination. In the following we assume, that the gas molecules which carry the nanoparticles do not contribute to the light scattering. This is certainly not correct, but we are only interested in the dynamic behavior of the scattered light. As long as the gas molecules can be considered as small compared to the particles their Brownian motion is much faster than that of the particles. The contribution of the molecular motion to the fluctuation of the scattered light field is therefore on a much shorter time scale than the fluctuation caused by the particle motion. The neglection of the molecular scattering is therefore justified as long as the particles can by considered as large compared to the size of the molecule.

We further assume that their is no interaction between the particles, so that the light scattering process on each particle can be considered as independent of all others. Finally we restrict our self to homodyne scattering, which means only light scattered from the particles hits the detector.

If the particles are exposed to coherent light, the partial waves scattered on the individual particles interfere on the light sensitive area of the detector. The resulting field depends on the scattering geometry and the particle position in the scattering volume. The scattering geometry can be considered as time independent, but not the particle position. As the particle position changes in time the interference pattern of the coherently superimposed partial waves changes as well and causes a time varying detector signal. The distance between scattering volume. Therefore, the effect of changes in the scattering angle or the particle distance to the detector can be neglected and the phase variations of the partial waves are governed by changes in the relative position of the particles to each other and in some cases by the local variation of the incident laser field. The situation is illustrated by Fig. 2, which shows the change in the interference pattern due to variations of the relative particle position and changes in the intensity of the scattered light caused by the displacement of the particles in the laser beam with its space dependent intensity profile.



Fig. 2. Variation of the interference pattern generated by coherent superposition of the scattered partial waves as function of interparticle distance and position in the Laser beam.





3 Mathematical description

3.1 Static case

Following Berne and Pecora (1976) the heterodyne time autocorrelation function of a detector exposed to a light field with amplitude E_s is linearly proportional to the function I_2 , which is given by

$$I_2(t) = \left\langle \left| E_s(0) \right|^2 \cdot \left| E_s(t) \right|^2 \right\rangle \tag{1}$$

 $E_{\rm s}$ is the electrical field generated by coherently superimposing all partial waves impinging on the detector.

$$E_s(t) = \sum_{j=1}^{N} A_j \cdot \exp(i\mathbf{q} \cdot \mathbf{r}_0 \cdot (t)) \cdot P(\mathbf{r}_0 \cdot (t))$$
(2)

The scattering amplitude of the particles is designated by A_j ; $\mathbf{q} = \mathbf{k}_{inc} - \mathbf{k}_{sca}$ is the scattering vector, whose amplitude is given by

$$q = \frac{4\pi n}{\lambda} \sin\frac{\Theta}{2} \tag{3}$$

where λ , *n* and Θ are the wavelength, refractive index and scattering angle respectively. *P*(*r*) is the power density of the laser beam. Eq.(2) introduced in Eq. (1) yields

$$I_{2}(t) = \langle \sum_{j,k,l,m} A_{j} \cdot \exp(i\mathbf{q} \cdot \mathbf{r}_{j}(0)) P(\mathbf{r}_{j}(0))$$
$$\cdot A_{k} \exp(-i\mathbf{q} \cdot \mathbf{r}_{k}(0)) \cdot P(\mathbf{r}_{k}(0)) \cdot A_{l} \exp(i\mathbf{q} \cdot \mathbf{r}_{l}(t))$$
$$\cdot P(\mathbf{r}_{l}(t)) \cdot A_{m} \cdot \exp(-i\mathbf{q} \cdot \mathbf{r}_{m}(t)) P(\mathbf{r}_{m}(t)) \rangle$$
(4)

In most cases one can safely assume, that the characteristic dimension of the scattering volume is much larger than the diffusive displacement for times comparable to the experimental correlation time. In this case the time average over the diffusion term and the position term can be separated and one can put $P(r(0)) \cong P(r(t))$.

$$I_{2}(t) = \sum_{j,k,l,m} \left\langle A_{j}A_{k}A_{l}A_{m} \cdot \exp\left[i\mathbf{q}\left(\mathbf{r}_{j}(0) - \mathbf{r}_{k}(0)\right) + \mathbf{r}_{l}(t) - \mathbf{r}_{m}(t)\right] \right\rangle \cdot \left\langle P\left(\mathbf{r}_{j}(0)\right) \cdot P\left(\mathbf{r}_{k}(0)\right) \cdot P\left(\mathbf{r}_{k}(0)\right) \cdot P\left(\mathbf{r}_{m}(t)\right) \right\rangle$$

$$(5)$$

Due to the statistical independence of the particles the ensemble average will be zero if any of the four indices is distinct. Therefore only the following two terms survive, j = k and l = m including j = k = l = m

$$I_{2a}(t) = \sum_{j,l} \left\langle A_j^2 \cdot A_l^2 \right\rangle \left\langle P^2(\mathbf{r}_j(0)) \cdot P^2(\mathbf{r}_l(t)) \right\rangle$$
(6)

and the term j = m, k = l, $j \neq k$

$$I_{2b}(t) = \sum_{j,k} \left\langle A_j^2 \cdot A_k^2 \cdot \exp\left[i\mathbf{q}\left(\mathbf{r}_j(0) - \mathbf{r}_j(t)\right) - \left(\mathbf{r}_k(0) - \mathbf{r}_k(t)\right)\right] \right\rangle \left\langle P^2\left(\mathbf{r}_j(0)\right) P^2\left(\mathbf{r}_k(t)\right) \right\rangle$$
(7)

If the displacement $\mathbf{r}_{i}(0) - \mathbf{r}_{i}(t)$ is governed by diffusion Eq.(7) reads

$$I_{2b}(t) = \left\langle \sum_{j,k} A_j^2 A_l^2 \exp\left(-q^2 \left(D_j + D_k\right) \cdot t\right) \right\rangle \left\langle P^2(\mathbf{r}_j) P^2(\mathbf{r}_k) \right\rangle$$
(8)

where D is the particle diffusion coefficient.

The evaluation of the sums yields finally

$$I_{2} = I_{0}^{2} \left[\left\langle A^{4} \right\rangle \left\langle N \right\rangle + \left\langle N(N-1) \right\rangle \left\langle A^{2} \right\rangle^{2} + \left\langle N(N-1) \right\rangle \left\langle \sum_{i,j} A_{j}^{2} A_{i}^{2} \exp\left(-q^{2} \left(D_{j} + D_{i}\right) t\right) \right\rangle \right]$$

For a sufficient number of particles one gets

$$I_{2} = I_{0}^{2} \left[\left\langle A^{4} \right\rangle \left\langle N \right\rangle + \left\langle N(N-1) \right\rangle \right] \left[\left\langle A^{2} \right\rangle^{2} + \left(\int A^{2} f(A) dA \cdot \exp(-qtD(A)) \right)^{2} \right]$$
(9)

where $\langle N \rangle$ represents the mean particle number in the scattering volume and the summation was replaced by the scattering cross section weighted by its frequency of occurrence f(A).

It is common practice to use the intensity scattering cross section Q in place of the square of the scattering amplitude $\langle A^2 \rangle$ and Eq. (9) reads, if the particle number concentration is described by Poisson statistics

$$\frac{I_2}{I_0^2} = \left\langle Q^2(a) \right\rangle \left\langle N \right\rangle + \left\langle N \right\rangle^2 \left[\left\langle Q \right\rangle^2 + \left| \int Qf(Q) dQ \exp\left(-q^2 D(Q) \cdot t\right) \right|^2 \right]$$
(10)

The scattering cross section Q and the diffusion coefficient D depend on the particle size a.

3.2 Dynamic case

We now consider a situation were the aerosol particles are not only subject to Brownian motion but are also conveyed by a macroscopic flow with velocity u through the laser beam. In this case the vector r(t) of the particle position is given by

$$\mathbf{r}(t) = \mathbf{u} \cdot t + \mathbf{r}'(t) \tag{11}$$

In Eq. (11) the particle displacement is composed of a convective term *ut* and a random motion r'(t) due solely to the diffusion. Usually the distance *ut*, where *t* is in the order of the correlation time τ , is not small compared to the laser beam diameter and the change in the local laser intensity has now to be taken into account. if a laser operates in the TEM₀₀ mode its field profile is given by

$$E(\mathbf{r}) = E_0 e^{-\frac{r^2}{w^2}}$$
(12)

where w is the radius of the beam waist.

The electric field of the scattered wave is now given by

$$E_{s}(t) = \sum_{j=1}^{N} A_{j} \exp\left(i\mathbf{q} \cdot \left(u \cdot t + \mathbf{r}'(t)\right)\right) E_{0} \cdot \exp\left(-\frac{\left(\mathbf{u} \cdot t + \mathbf{r}'(t)\right)^{2}}{w^{2}}\right)$$
(13)

The diffusive displacement $\mathbf{r}'(t)$ can be neglected against the convective term $u \cdot t$ in the last factor of Eq. (13). This expression has to be introduced into Eq. (5). Evaluating this equation as before yields finally, to

$$\frac{I_2(t)}{I_0} = \langle N \rangle^2 \left[\langle Q \rangle^2 + \exp\left(-\frac{u^2 t^2}{w^2}\right) \cdot \left| \int Q f(Q) dQ \exp(-D(a)q^2 \cdot t) \right|^2 \right]$$
(14)

$$\gamma \cdot \langle Q^2 \rangle \langle N \rangle \exp\left(-\frac{u^2 t^2}{w^2}\right)$$

where γ is a factor which depends on the shape of the scattering volume.

For monodisperse particles this equation simplifies to

$$\frac{I_2(t)}{I_0} = \langle N \rangle^2 \left[1 + \exp\left(-\frac{u^2 t^2}{w^2}\right) + \exp(-2Dq^2 t) \right] + \gamma \langle N \rangle \exp\left(-\frac{u^2 t^2}{w^2}\right)$$
(15)

This equation was first given by Chowdhury et. al. (1984). This result implies complete coherence of all partial waves. For the more realistic case one has to include the effect of

finite aperture angle, which reduces the degree of coherence and one gets, Weber et. al. (1993),

$$\frac{I_2(t)}{I_0^2} = \langle N \rangle^2 \left[1 + f(A) \cdot \exp\left(-2Dq^2t\right) \cdot \exp\left(-\frac{u^2t^2}{\omega^2}\right) \right]$$

$$+\gamma \langle N \rangle \exp\left(-\frac{u^2t^2}{w^2}\right)$$
(16)

where the degree of coherence can be estimated by the relation

$$A_c = \frac{\pi}{4} (\Delta r)^2 = \frac{\pi}{4} \left(\frac{\lambda \cdot R}{2\pi\rho} \right)^2 \tag{17}$$

In contrast to the work of Chowdhury et. al. Weber et. al. (1993) investigated the effect of small numbers of particles in the scattering volume. This aspect was recently investigated by Itoh and Takahashi (1991) for a non flowing aerosol.

If the particle concentration is low, the last term on the right side of equation (16) cannot be neglected.

Using the following abbreviations:

$$\tau_1 = \frac{1}{2q^2 D}, \quad \tau_2 = \frac{u}{\omega}, \qquad \xi = \frac{\gamma}{f(A) \cdot \langle N \rangle}, \tag{18}$$

equation (16) can be written as follows:

$$\frac{I_2(t)}{I_0^2} = \langle N \rangle^2 \left[1 + f(A) \cdot \left(\overline{e}^{t/\tau_1} + \xi \right) \cdot \overline{e}^{\frac{t^2}{\tau_2^2}} \right]$$
(19)

Subtraction of the DC component and normalization yields:

$$i_{2}(t) = \frac{I_{2}(t) - I_{0}^{2} \langle N \rangle^{2}}{I_{2}(0) - I_{0}^{2} \langle N \rangle^{2}} = \frac{e^{-t/\tau_{1}} + \xi}{1 + \xi} e^{-t^{2}/\tau^{2}}$$
(20)

A convenient method to evaluate the correlation function is its representation on a semi logarithmic plot

$$y(t) = \frac{1}{t} \ln(i_2(t)) = \frac{1}{\tau_2^2} - \frac{1}{t} \ln \frac{e^{-t/\tau_1} + \xi}{1 + \xi}$$
(21)

In the Gaussian case the mean particle number $\langle N \rangle$ in the scattering volume can be considered as so large that ξ is much smaller than one, and equation (21) transforms into the familiar form:



Fig. 4. Effect of ξ on the semilogarithmic representation of the autocorrelation function shown in Fig. 3.





$$y(t) = \frac{t}{\tau_2^2} + \frac{1}{\tau_1}$$
(22)

The parameter ξ depends, as shown by equation (18), on the aperture angle via the coherence function f(A) and on the particle number concentration as well as on the size of the scattering volume. Both, the particle number concentration and the size of the scattering volume, determine the mean particle number $\langle N \rangle$ in the scattering volume.

Fig. 3 shows the effect of ξ for a fixed τ_1 and τ_2 on $i_2(t)$ and Fig. 4 its logarithmic form. The relatively strong effect of ξ especially at small values is obvious.

4 Data Inversion

Probably the most serious problem in the application of dynamic light scattering for particle analyses is the extraction of the particle size from the correlation function or its Fourier transform, the power spectrum of the scattered light. The correlation function (power spectrum) is recorded over a relatively long period of time compared to the characteristic time scale of the fluctuations in the scattered light field. As a consequence the recorded function (power spectrum) contains only information of the average time behavior of these fluctuations. Due to the averaging procedure inherent in the recording procedure, information is lost or buried in detector noise, which has to be provided somehow to the inversion algorithm. Without this information the various inversion algorithms are more or less useless. In most cases this information is provided by some restrictions imposed to the solution of the various inversion algorithms. The most widely used restrictions are, that only a certain particle size range and only positive contributions to the size distribution are accepted. An other frequently used constraint is, that only the smoothest distribution of the solution manifold is accepted as the "true" solution.

Mathematically the inversion problem boils down to the solution of a Fredholm integral equation of the first kind.

$$g(x) = \int_{a}^{b} K(x,a) \cdot f(a) da$$
(23)

In the case of photocorrelation the kernel is given by

$$K = \exp(-q^2 D(a)x) \tag{24}$$

and in the frequency domain, where the line shape of scattered light is measured, the kernel is given by

$$K = \frac{q^2 D(a)}{x^2 + q^2 D^2(a)}$$
(25)

This is a problem which belongs to the class of ill-posed problems, which means minor changes in g(x) can lead to large deviations in the solution of Eq. (23). This means if $f_0(a)$ is a solution of

$$g_0 = \int_a K(k,a) f_0(a) da$$

and $f_1(a)$ a solution of

$$g_0 + \Delta g = \int_a^b K(x,a) f_1(a) da \qquad \Delta g \ll g_0$$
(27)

(26)

 f_1 can be very different from f_0 . In an experimentally determined correlation function there is always noise. The equation which has to be solved is therefore

$$g_{ex}(x) = \int_{a}^{b} k(x,a) \cdot f(a) da + noise$$
⁽²⁸⁾

Due to the presence of noise their is no unique solution to Eq.(23) Additional information is necessary to pick the most probable solution from the family of possible solutions.

Despite this principal problems, the distribution calculated directly from the recorded data is the distribution from the scattered light intensity. A theoretical model to transform the intensity distribution to the size distribution is necessary. For particles in the nanosize range the intensity of the scattered light is proportional to the sixth power of the particle radius. A few large particles contribute easily as much to the scattered light as a high number of small particles. In terms of intensity, the large particles are highly over represented in the scattered light.

A number of different inversion procedures exist today and are summarized in various review articles (Finsy et. al. (1992), McNeil-Watson et. al. (1991), Stock and Ray (1985)). Most of this methods follow the following general guidelines (Provencher (1982)).

The Fredholm integral equation is discretizised

$$g_k = \sum_m c_m k_k(a_m) f(a_m) = \sum_m A_{km} \cdot f_m$$
⁽²⁹⁾

because the correlation function is also determined in discrete time steps. Then some constraints are imposed on the solution. For example that size frequency must be positive and extends only over a given size range $a_m \le a_m \le a_{ma}$.

Finally the solution is subject to regularizations, a very popular one is that smooth solutions are more likely than peaked solutions.

This bias for smooth solution can be selected by a regularization parameter

$$\left\|M_{\varepsilon}^{-1/2}\left(g-Af\right)\right\|^{2} + \alpha^{2} \int_{a}^{b} \left[f''(a)\right]^{2} da = \text{minimum}$$
(30)





(Lhuissier, N., Goueshet, G., and Weill, M.E. (1989)).





(Zachariah et. al (1989)).

Where M_{ϵ} is the covariance matrix of the $\epsilon_{k,g}$ is a $N_{g} \times 1$ vector with elements g_{κ} and $\|\cdot\|$ is the Euclidean norm. In the case of a flowing aerosol non of the existing methods is applicable directly to the correlation function. The philosophy tested by the author is therefore the following: Eq. (14) is transformed into a similar form as Eq. (20) which was developed for the monodisperse case. The convection velocity, respectively the transit time τ_{2} is determined independently and the equation multiplied by $\exp(-t^{2}/\tau_{2}^{2})$. The result is free from the convective term and ready to be solved by one of the conventional techniques.

Preliminary results indicate that the size determination depends sensitively on the accuracy of τ_2 .

5 Application

By far most of the applications in photon correlation spectroscopy were done in liquids, liquid suspensions or colloids. One of the reasons is undoubtedly the great interest in the determination of transport properties and properties of the suspended material in such systems. Only a dozen or so papers have appeared in the last two decades, where this technique was used to investigate aerosols. Compared with liquid suspensions the number density and therefore the scattered intensity is lower in aerosol systems and the correlation time is approximately two orders of magnitude lower for the same particle size. The coherence time for a scattering angle of 90° is shown in Fig. 5 as a function of the geometrical diameter of particles suspended in air. Both effects increase experimental problems.

The main area of application in aerosol systems was up to now the investigation of reaction processes. Hinds and Reist (1972), King et al. (1982), Weill, Flament, and Gouesbet (1983), Scrivner et al. (1986), Lhuissier, Nazih, and Weill (1988) as well as Lhuissier, Gouesbet and Weill (1989) Zacharias et al. (1989) used dynamic light scattering to investigate the formation of soot particles in combustion processes. The investigations were made in the size range from approximately 10 nm to several hundred nanometer in some cases. When polydisperse particles were considered, the validity of the Rayleigh theory was assumed. Hinds and Reist (1972) and Weill, Flament, and Gouesbet (1983) measured only the power spectrum of the scattered light by an electronic spectrum analyzer, whereas Scrivner et al. (1986) and Lhuissier, Nazih, and Weill (1988) recorded only the auto correlation function. Lhuissier, Gouesbet and Weill (1989) determined the power spectrum of the scattered light by an electronic spectrum analyzer and the time autocorrelation function by a digital correlator. The effect of convective motion was included in the theoretical analyses but the experimental conditions were chosen so that this effect could be neglected or the velocity was assumed to be known (Weill, Flament, and Gouesbet (1983)).

Dynamic light scattering was also applied to investigate the formation of ultrafine particles by gas phase reactions by Flower and Hurd (1987) and Hurd and Ho (1989, 1991).

Typical results are shown in Fig. 6 and Fig. 7. Fig. 6 shows the diameter of silicon particles formed by flame synthesis as function of the distance from the center. The results are compared with particle diameters determined by Mie-scattering. The particle diameters were calculated from the power spectrum assuming a monodisperse size distribution. Fig. 7 shows the diameter of soot particles as function of the distance from the burner. The diameters were determined from the time auto correlation function as well as by evaluation of the power

spectrum of scattered light. In both cases the indicated particle size was found by assuming a monodisperse aerosol.

6 Conclusion

Dynamic light scattering has its main field of application in colloidal sciences, where recent comparative studies show that this techniques is a powerful method for the determination of particle sizes in the nano size regime (De Jaeger et al. (1991). However the data inversion becomes increasingly difficult and unreliable if the size distribution is complicated. A large number of efforts was invested in the development of inversion procedures. Some of the available methods, for example Provenchers regularization technique yield very satisfactory results for smooth monomodal distributions but have problems with multimodal distributions. If several modes are present exponential sampling is more capable to recover the size distribution. In all cases an a priori knowledge is necessary.

The application of this technique in aerosol science is in a rather early stage. One of the reasons is that the diffusion coefficient for a given particle size suspended in a gaseous medium is about two orders of magnitude larger than in a liquid. For particles in the order of 10 nm the correlation time is at 90° scattering angle typically 10 ns. Modern digital correlators have a time resolution of 20 ns. The measurement of the time auto correlation is therefore difficult. Alternatively the line width of light elastically scattered on a 10 nm particle is typically 16 MHz. The measurement of such narrow line width is possible however not trivial.

Dynamic light scattering experiments in an laminar aerosols flow can be made successfully as long as the flow is laminar. Only some preliminary results are available for turbulent flows.

As a summary the determination of aerosol particle size distributions in the nanometer size range is possible, but information on the absolute size of the particles have to be checked critically, but for an on line noninvasive size determination in the nanometer range not many alternatives are in sight.
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On-Line Measurement of Magnetic Properties of Aerosol Particles

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1.Introduction

Particles with a remanent magnetization, magnetic particles, are used in production of memory devices such as audio and video tapes and computer memories. They are also required for new magnetic working materials. Aerosol routes have an increasing potential in generation of such particles, (Biswas). We anticipate that the importance of these aerosol routes in industrial processes will increase in the future.

The magnetic properties of the particles are a function of the raw material and the generation conditions. In addition, they are strongly dependent on the particle size. In the size range from submicron particles down to ultrafine particles the magnetic properties change very strongly with particle diameter, (H.Jakusch and R.J.Veitch). Fig.1 shows the induced magnetization M versus the magnetic field applied.



fig.1 The particle magnetization versus the field strength

The coercitive force i.e. the field required to change the direction of magnetization (intersection of the curves in fig.1 with H-axis) is shown as a function of particle size in fig.2, (H.Jakusch and R.J.Veitch).



fig.2 The coercitive force versus the particle size

Below a critical diameter dp_{e1} there is no remanent magnetization of the particles. They are called superparamagnetic and are useless for storing information. Above dp_{e1}

formation of a single magnetic domain becomes possible. In this range the arrangement of atomic dipoles changes with particle structure and size to form the state of lowest energy. Above dp_{c2} energy minimization leads to formation of several domains. These particles are called multi-domain particles. A high coercitive force is desirable for memory devices.

We introduce the first measurement technique allowing on-line and in situ measurement of the magnetic properties of aerosol particles. It responds to micromagnetism of noninteracting particles rather than the collective magnetization of a powder. Combined with aerosol methods of sharp size classification it provides new possibilities for basic research on magnetic particles, as well as a tool to control and optimize magnetic particle generation.

2. The new measurement technique

The main part of the measuring system is an aerosol filter with magnetizable fibers, (Th.Kauffeldt and A.Schmidt-Ott). These can be magnetized by an external homogeneous coil field. In the proximity of a magnetized fiber there is a strong field gradient. This causes a magnetic dipole force pulling particles to the fiber. The penetration of this magnetic filter decreases when the magnetic force increases. This force is a function of particle magnetization and fiber magnetization. The measured value is filter penetration.



fig.3 The new measuring device

The measurement principle is illustrated in fig.4. The filter is a screen-type diffusion battery, (Y.S.Cheng and H.C.Yeh). The screens consist of woven nickel-fibers with a diameter of 50 μ m and a spacing of 56 μ m. By varying the coil current the external magnetic field and therewith the fiber magnetization can be changed. The number concentrations at the inlet and the outlet of the magnetic filter are measured by UCPC's (Ultrafine Condensation Particle Counters). The ratio of their concentrations, the penetration, is continuously calculated by a computing unit.

3. Theory

The filter characteristic depends on diffusion and forces and is given by the following equation for the Penetration (P), (Y.S.Cheng and H.C.Yeh), (Lathrache et.al).

$$P = \exp\left(\frac{-2A(\alpha)h}{\pi(1-\alpha)d_f} \left(1-(1-\gamma_d)(1-\gamma_m)\right)\right), \qquad (1)$$

with α the packing density, A(α) a function of the packing density, h the filter length, d_f the fiber diameter and γ_d and γ_m the single fiber efficiencies due to diffusion and the magnetic force, respectively. Diffusion is the dominant deposition mechanism for the measurements shown here. The magnetic force is

$$F_{maon} - \nabla / H/m \tag{2}$$

for perfect alignment of the particle magnetic moment m = M V (V = Volume) with the field H. Due to Brownian rotation, m in eq.(2) must be regarded as a time average of the component m parallel to the field. The single fiber efficiency due to the magnetic force is, in analogy to electret filters, (Lathrache et.al.) a function of the ratio of the magnetic force and the drag force.

$$\gamma_m - f(\frac{B \ m \ \nabla/H}{v}) \tag{3}$$

Here m is the magnetic moment of a particle, B the mobility and v the flow velocity. In absence of magnetic forces ($\gamma_m = 0$), γ_d can be determined from penetration through eq.(1). When magnetic forces are present, eq.(1) yields γ_m .

4. Test Aerosol Generator



fig.4 Test aerosol generator

The generator principle is outlined in fig.4. A colloidal Suspension of Fe_2O_3 particles in H_2O is atomized (Möller et.al. 1990). After drying in a diffusion dryer, the aerosol is passed through a tube furnace in which the particles are converted to a magnetic iron oxide (presumably ferrimagnetic γ -Fe₂O₃ or Fe₃O₄). After reduction a defined particle

charge distribution is established in a radioactive neutralizer. A monodisperse fraction is taken out by a Reischel-type differential mobility analyzer (DMA). By bypassing the tube furnace, the system delivers paramagnetic Fe_2O_3 particles. The critical parameters of this generator are reaction temperature, reaction time in the tube furnace and gas composition. Nitrogen of purity 5.0 has been used in all measurements reported here. To yield strongly magnetic particles, optimization of this generator is the first application of our new measuring system, to be described in the following.

5. Experimental Results

5.1 Determination of the fraction of magnetic particles in an aerosol

The first application was to find the generator conditions for which all particles are reduced into the magnetic iron oxide. We developed a filter with 100% retention of magnetic particles. This 100%-filter has zero penetration for particles that are reduced to the magnetic form. It consists of a copper tube filled with ferromagnetic steel wool. For non-magnetic Fe₂O₃ particles penetration was independent of the coil current (i.e. fiber magnetization). Incomplete conversion to a magnetic oxide in the tube furnace leads to penetration of this particle fraction. This penetration became independent of the coil current above a certain value confirming that all magnetic particles are kept back by the filter. Knowing the penetration for non-magnetic (paramagnetic) particles P_{para} and converted particles P_{conv} the fraction f of particles converted into a magnetic oxide is $1-P_{para}/P_{conv}$.

To determine the temperature of the reduction furnace at which all particles are converted we increased the furnace temperature slowly and measured the output concentration of our 100%-filter. In figure 5 the converted fraction is plotted versus the furnace temperature.

5.2 Optimizing the generator parameters

The magnetic moment of those particles converted into a magnetic oxide depends on the conditions in the reducing furnace. Our aim was to obtain particles of the highest possible m. The no. of screens in the magnetic filter and the coil current were chosen such that the dynamic range of P was adequate to observe the effect of



fig.5 The fraction of particles converted to a magnetic iron oxide

generator conditions on m. We found that addition of H_2 as a reducing agent (as used by Möller et al.) does not lead to higher m. The optimum reduction time, controlled by flow velocity and tube furnace volume, was about 3s. Contamination of the quartz tube in the furnace leads to a slow reduction of m in the course of time.

5.3 Measurement of penetration as function of particle diameter

Fig.6 shows the penetration data for non-magnetic particles pure diffusion and magnetic

particles at different coil currents, i.e. fiber magnetizations as a function of the particle diameter. For all sizes investigated there is a measurable magnetic effect on penetration, as comparison with the non-magnetic case (pure diffusion) shows. With increasing diameter and particle mass, an increase in the magnetic force, causing a decrease in penetration can

he observed.

To get a measure of the magnetic moment it is necessary to separate the influences of mobility B and magnetic moment m. We therefore performed an experiment in which particles with constant m and variable B are used.



fig.6 The filter penetration for different fibermagnetization versus the particle diameter

5.4. The influence of mobility on magnetic single fiber efficiency

The first DMA in fig.7 was set to a constant voltage yielding particles of 70nm. This



fig.7 The experimentall set up for determination of the influence of the mobility

aerosol was bubbled through a tempered DES-bath (Bis 2-ethylhexyl sebacate). The DES vapour pressure was controllable via temperature. With the aerosol flowing through a cooled tube, vapour condenses on the particles. These coated iron oxide particles are separated from the homogeneously nucleated DES particles by a second DMA. By varying the temperature of the bath, the particle mobility is variable with the constant magnetic moment of the nucleus maintained. The results are shown in figure 8. Here the magnetic single fiber efficiency is plotted versus mobility for different fiber magnetizations represented by different coil currents. For each fiber magnetization there is a range of single fiber efficiencies roughly proportional to B. According to eq.(2) this



fig.8 The magnetic single fiber efficency versus the particle mobility

means that the ratio of single fiber efficiency and mobility is proportional to the magnetic moment. For small fiber magnetizations this relationship is quite precise. The measurement above yields the relation between γ_m and B. According to eq.(3) this is also the relation between γ_m and F_m , since F_m and B only appear as a product. Due to $F_m \propto m$, we now have an empirical relation $m(\gamma_m)$, apart from a constant.

5.5. The magnetic moment of ultrafine particles versus the diameter

Using the proportional region of the graph in fig.8 the magnetic moment of particles was



fig.9 The magnetic moment versus the particle diameter

calculated by dividing the measured single fiber efficiency through the mobility of the particles. The result is shown in figure 9, the magnetic moment is plotted in arbitrary

units. The non-monotonic behaviour is surprising. Possibly there is a phase transition in the magnetic domain structure.

6. Sensitivity of the present set-up

The smallest magnetic particle diameter producible with our generator in a number concentration sufficient for our measurement was 13nm. For 13nm we calculate an upper limit of $m = 6 \cdot 10^{-19} \text{ Am}^2$, by assuming 4 Bohr magnetons per atom and a density of 5 g/cm³ and a single magnetic domain. The effect of the magnetic moment of these particles on penetration was 35% as comparison with the non-magnetic case showed. Considering that 5% would be resolvable, our measurement detects at least magnetic moments of 8 10^{-20} Am^2 . For a good statistics we require at least 10^4 particles, or a total magnetic moment of $8 \cdot 10^{-16} \text{ Am}^2$. The true magnetic moment of our 13nm particles is probably much lower than the value assumed and considerable improvements of the measurement technique can be made (e.q. by increase of fiber magnetization). A detection limit of $5 \cdot 10^{-18} \text{ Am}^2$ seems feasible.

7. Conclusions

We developed a new measuring technique for measurement of micromagnetism. An interesting application is optimization of magnetic aerosol particle generators. The fraction of magnetic particles in an aerosol can be determined. A relative measure of m can be determined from the magnetic single fiber efficiency by means of an empirical relation. The measurement could be calibrated by comparison with standard techniques. The estimated detection limit of the measured magnetic moment (5 10^{-18} Am²) is much lower than the sensitivity of modern SQID devices (~ 10^{-14} Am²).

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ULTRAFINE PARTICLES IN ATMOSPHERIC ELECTRICITY

Hannes Tammet Tartu University

The ultrafine particles are called air ions in atmospheric electricity. The paper deals with traditional and new classification of air ions in atmospheric electricity and tools of ion-particle parameter conversion. The problem of clusterparticle discrimination is examined. A brief overview of the atmospheric electrical particle measurement techniques is presented. Some results of atmospheric electrical measurements of particle size distribution and the role of ultrafine particles in the atmospheric electricity are discussed.

INTRODUCTION

The mechanism of electrical conductivity of air is a classic research subject in atmospheric electricity (Israel, 1970). The carriers of electrical current in air are charged airborne particles of size of 0.5-200 nm and their evolution is influenced by neutral airborne particles. The cooperation of aerosol and atmospheric electricity research is providing both sides with some extra knowledge.

The first measurements of air ion mobility were made by J.J. Thomson and Rutherford (1896) in a laboratory experiment. According to the contemporary interpretation, they have studied charged clusters of diameter of 0.6-0.7 nm. The air ions of low mobility and large size were measured by Townsend (1898) and Lenard (1900) in laboratory experiments and by Langevin (1905) in natural atmospheric air. The diameter of air ions measured by Langevin was about 90 nm and they are often called the Langevin ions today. First measurements of intermediate air ions (diameter about 10 nm) were published by Pollock (1915).

An overview of ultrafine particle related concepts and methods of groundlevel atmospheric electricity research and a digest of measurement results obtained in Tartu University is presented in the paper.

AIR IONS AND AEROSOL PARTICLES

Classification of air ions

Carriers of conductive current in the air are called the atmospheric ions or the air ions independent of their physical nature. They can be molecular ions, charged clusters, solid or liquid airborne particles of any size. The parameter of an air ion that can be reliably measured using standard techniques of atmospheric electricity is the electrical mobility K = v/e, where v is the drift velocity of the air ion and E is the intensity of the electric field.

Traditionally, the air ions are classified according to their electrical mobility:

fast or small or light ions with mobility $K > 0.5 \text{ cm}^2/(V \cdot s)$, intermediate ions, and slow or large or heavy ions with mobility $K < 0.01 \text{ cm}^2/(V \cdot s)$. The boundary between small and intermediate ions has a physical background but the boundary between intermediate and large ions is a convention.

The alternate classification is based on the physical nature of air ions:

cluster ions are charged clusters,

aerosol ions are charged ultrafine and fine particles.

The problem of discriminating between clusters and ultrafine particles will be discussed later.

In a primary act of ionization a free electron and a positive molecular ion are created. The lifetime of free electrons and molecular ions in natural air is very short and their role in the ground-level atmospheric electricity is negligible. The average lifetime of a cluster ion is one minute. About 3% of them will recombine with cluster ions of another polarity and 97% will attach to aerosol particles. Resulting aerosol ions are called the secondary aerosol ions. The primary aerosol ions are the particles with inherent electric charge that are formed as a result of ion-induced nucleation. The secondary aerosol ions are dominating among all aerosol ions.

The aerosol ions could be classified as ultrafine and fine aerosol ions according to the particle size.

Size-charge relation for particles

The cluster ions are never considered in uncharged state. A particle of the diameter of less than 30 nm in the bipolar ionic atmosphere is neutral or charged by one elementary charge. There is no reliable empirical data available about size-charge relation for nanometric particles. Well-founded theoretical calculations of ion-particle attachment coefficients are published by Hoppel and Frick (1990). The coefficients have been essentially depending on the mass of cluster ions. Probably, Hoppel and Frick have slightly overestimated the mass of positive ions and underestimated the mass of negative ions for average atmospheric conditions. When the average over both polarities is used, a simple approximation for the particles of the diameter of less than 30 nm can be derived and recommended as a tool for practical calculations:

$p = 0.0065d_{m} + 0.024/(d_{m}+0.3) - 0.018,$

where d_{nm} is the numerical value of the diameter expressed in nanometers and p is the probability of carrying an elementary charge of one polarity. The probability of being neutral is 1 - 2p. The relative error of the approximation is less than 6% for the particles of the diameter of less than 20 nm.

An approximation for larger particles based on the tables by Hoppel and Frick has been published in (Tammet, 1991).

Mobility-mass conversion tools for clusters

The mobility and mass of cluster ions can be measured simultaneously in laboratory experiments. A data set for ion mass from 35.5 up to 2122 u published by Kilpatrick (1971) is used by various authors. The data can be fitted by formulas:

$$K_{\rm cm} = (850/m_{\rm p})^{1/3} - 0.3, \qquad m_{\rm p} = 850/(K_{\rm cm} + 0.3)^3$$

where K_{cm} and m_u are the numerical values of mobility and mass expressed in $cm^2/(V \cdot s)$ and u. The mean-square relative fitting error is 3.2%.

Size-mobility conversion tools for particles and clusters

The Millikan equation is an excellent approximation of the size-mobility relation for fine particles. It can be modified to cover the whole range of fine particles, ultrafine particles and clusters (Tammet, 1992). In case of normal air pressure and room temperature the following algorithm can be used:

$$F = 0.5 \cdot \exp(-\left(\frac{d_{\text{nm}}}{1.32}\right)^6), \qquad G = \sqrt{\left(1 + \left(\frac{0.4}{d_{\text{nm}}}\right)^3 / \left(1 + \left(\frac{0.7}{d_{\text{nm}}+0.73}\right)^4\right),$$
$$K_{\text{cm}} = \frac{0.00943}{d_{\text{nm}}+0.73} \left(1 + \frac{129}{d_{\text{nm}}+0.73} \left(1.4 + 0.35 \cdot \exp\left(-\frac{d_{\text{nm}}+0.73}{144}\right) + F\right)\right) G.$$

The correction G is essential only when d < 1 nm and the correction F when d < 1.7 nm. In case of larger particles the above algorithm is the same as the ordinary Millikan formula where the diameter is replaced by d + 0.73 nm considering the size of air molecules and Van der Waals forces. The algorithm

$$a = 4 + \exp(-3/(\sqrt{(1 + 93000K_{cm}) - 1)}),$$

$$d_{\rm m} = 90a / (\sqrt{(1 + 19060aK_{\rm m})} - 1) - 0.73$$

is inverting the above algorithm with relative error less than 0.15% for all diameters over 1.8 nm.

In the size range of 1.7-260 nm the above K = K(d) algorithm is approximated by simple formulas with error of K_{cm} less than 0.32% and of d_{nm} less than 0.2%:

$$K_{\rm cm} = \left(\frac{2}{1 + d_{\rm nm}/0.73} + 0.0023\right)^2,$$

 $d_{\rm nm} = 0.73 \left(\frac{2}{\sqrt{K_{\rm cm}} - 0.0023} - 1 \right).$

Distinction between clusters and particles

The clusters and fine particles can be discriminated considering the applicability of various models of their internal physical structure. An external distinction is that the particles can be characterized by the internal temperature and they can absorb the energy of colliding air molecules but molecules and clusters cannot. The result is that the air molecules are thermally accommodated when colliding with particles and elastically scattered by clusters. It follows that a factor in the drag equation derived according to the Chapman-Enskog kinetic theory is different for clusters and particles. The fitting of the data presented by Kilpatrick (Tammet, 1992) was successful when the collisions were considered in case of d < 1 nm as elastic-specular and in case of d > 1.7 nm as accompanied by thermal accommodation. The critical diameter of 1.32 nm was found as a boundary separating clusters and ultrafine particles. The corresponding mass is 1300 u and mobility 0.5 cm²/(V·s).

MEASUREMENT TECHNIQUES

Drift tube and aspiration condenser

Drift tubes are the most popular instruments for measuring cluster ion mobilities in laboratory experiments. They have been used for measuring of ultrafine particles of size of up to 3 nm (B.A. Thomson and Iribarne, 1977). Too high driving voltage would be required for measuring larger particles. A drift tube can provide excellent mobility resolution if the cluster ions are generated inside the instrument and measured in the first milliseconds of their life. If the natural ions are studied, the resolving power is limited by the ratio of the full volume of the tube and the volume of the sample air where the ions are initially located. If the sample air volume in a large drift tube is about 1 liter and the ion fraction concentration is about 10 cm⁻³, the full charge of about 1 fC is near the noise level of a typical amplifier. Therefore, the drift tubes are not effective when the natural ions are measured.

The sample air is continuously sucked through an aspiration condenser that enables to collect the ions from a large air volume and keep the sensitivity of the instrument high enough to measure natural air ions. The aspiration condenser is an efficient instrument in the mobility range of $0.0003-3 \text{ cm}^2/(\text{Vs})$.

The integral and differential aspiration condensers

The simplest air ion meter known as Gerdien instrument is equipped with a cylindrical aspiration condenser, where the sample air is filling a full crosssection of the condenser and the current is measured from the full area of the collector electrode. The undivided aspiration condenser is called the integral condenser. It provides the best concentration sensitivity and the poorest mobility resolution. When the driving voltage is low, the collected current is proportional to the air conductivity. If the driving voltage is high and only small ions are present, the collected current is saturated and ion concentration is measured. The average mobility can be found as the ratio of air conductivity and ion concentration. The sophisticated analysis of the volt-ampere character-istic allows to calculate the mobility distribution of ions (Israel, 1970; Tammet, 1970). However, an enormous effect of "error amplification" prevents the real resolution of ions with the mobility ratio less than two.

The physical differentiation of the volt-ampere characteristic can be carried out dividing the air intake into a narrow layer of sample air and a wide layer of deionized air, and/or dividing the collector electrode and measuring the current only from a narrow section of the electrode. The corresponding versions of an aspiration condenser are called:

the first-order differential condenser with the divided air flow,

the first-order differential condenser with the divided electrode,

the second-order differential condenser.

The best mobility resolution is provided by the second-order differential aspiration condenser. Usually, the record of the volt-ampere characteristic of a second-order differential condenser is directly interpreted as a diagram of mobility distribution of the air ions. The differential condensers of first order were rarely used considering their simplified design.



Fig. 1. The ideal volt-ampere characteristics: a - the integral aspiration condenser, b - the first-order differential condenser with divided air flow, c - the first-order differential condenser with divided electrode, d - the second-order differential condenser. The total air flow is assumed to be 1000 cm³/s, and the total active capacitance of the collecting electrode 50 pF. The dividing proportions are assumed to be 20% + 80% for air flow as well for the electrode capacitance. The three diagrams are corresponding to:

dotted - 1000 cm⁻³ of d = 6.5 nm particles, dashed - 1000 cm⁻³ of d = 8.0 nm particles, continuous - 500 cm⁻³ of d = 6.5 nm and 500 cm⁻³ of d = 8.0 nm particles.

The ideal volt-ampere characteristics of various aspirations condensers are given in Fig. 1. Real volt-ampere characteristics are slightly smoothed by diffusion of the air ions and other disturbing factors (Tammet, 1970), and disfigured by the measurement noise. Therefore, the correct estimating of the mobility distribution is a complicated mathematical procedure even in case of the second-order differential condenser.

Scanning and multichannel techniques

Two alternate techniques of the mobility distribution measurement are used in the atmospheric electricity research. In case of scanning technique the aspiration condenser with one collector electrode is used and the volt-ampere characteristic is measured step by step. The driving voltage is changed by discrete steps in some instruments and continuously in the others. In case of continuous change a compensating capacitor and a bridge circuit are used to suppress the induction current that could exceed the measurement current in many orders of magnitude. In the scanning spectrometers designed in Tartu University the continuous change of the driving voltage is carried out using a RC-circuit with time constant of 10-30 s that automatically provides the required logarithmic scale of mobility.

The measurement time is considered as an essential factor when choosing the measurement technique. About one hour or more is needed to suppress the noise when measuring the natural air ion mobility distribution using the scanning technique. The parallel multichannel technique was introduced to accelerate the measurements and to reduce the specific errors rising with the sequential measurement of changing mobility distribution.

A multichannel instrument differs from the ordinary one-channel secondorder differential aspiration condenser by having the collecting electrode that has been divided into many sections each of which is simultaneously collecting the ions of various mobilities. The measurement time is reduced by the factor equal to the number of sections. The first multichannel instrument was built by Yunker (1940). However, the real advantages of the multichannel technique were not realized before creating an advanced mathematical model of the multichannel mobility spectrometer and computerization of the measurement process. Several multichannel instruments with up to 50 parallel channels have been designed in Tartu University (Matisen et al., 1992).

MEASUREMENTS OF ULTRAFINE PARTICLES IN ATMOSPHERIC ELECTRICITY

Cluster ions

During its lifetime a cluster ion collides with nearly 10¹² molecules. Thus the cluster ions can concentrate trace gases of very low concentration if they have an extra high electron or proton affinity. For example, Eisele (1986) demonstrated that a considerable fraction of cluster ions in the unpolluted atmosphere probably consists of a molecule derived from pyridine. Therefore, the chemical composition and the size of cluster ions are depending on the spectrum of the trace gases in the air and can vary in various locations and conditions.

The one-year continuous measurements of natural cluster ion mobilities were carried out at a sparsely populated village Tahkuse, Estonia (Salm et al., 1990). The average distributions presented in Fig. 2 are probably typical for the rural regions. Fine aerosol ions

Air ions of the diameter of over 10 nm are usually secondary aerosol ions. The results of early measurements are summarized by Israel (1970). Salm (1988) has calculated the mobility distribution corresponding the average of particle size distributions, measured during last decades by various scientists. The result is presented in wide bars in Fig. 3. The four-month averages of directly measured aerosol ion distribution (Salm et al., 1990) are presented in pin bars in the same figure. The accordance of the diagrams is confirming the applicability of the theoretical model used by Salm.







Fig. 3. Distribution of aerosol ions. The wide bars mark the fraction concentrations of elementary charges carried by particles according to the calculations by Salm (1988). The pin bars with heads + and mark average values of fraction concentrations for positive and negative aerosol ions measured in village Tahkuse, Estonia.

Ultrafine aerosol ions

The concentration of secondary aerosol ions of the diameter of few nanometers in the natural air is very low and these ions are not available for measurement using ordinary instruments. The enlarged concentration of ultrafine aerosols can be expected in extra situations when primary aerosol ions are intensively generated as a result of ion-induced nucleation. Therefore, the measurement of air ions in the mobility range of $0.1-0.5 \text{ cm}^2/(V \cdot s)$ can be considered as a method to obtain information about the role of ion-induced nucleation in the real atmosphere.

The first message about the ions of the 10 nm diameter by Pollock (1915) cannot be qualified as authentic. The paper by Pollock does not give any information confirming the reliability of measurements. It is possible that the conclusion made by Pollock was a result of misinterpretation of measurement errors.

The measurement data about ultrafine ions in the natural air are poor. The reasons for this are technical complications and the disadvantageous tradition to classify the air ions into groups of 0.1-1.0 and $1.0-\infty$ cm²/(Vs). The cluster ions are presented in both groups and the data have no unambiguous interpretation.

In Tartu University, Reinet (1958) has observed and analyzed many extra situations with enhanced concentration of 0.1-1.0 cm²/(Vs) air ions during annual continuous measurements in the center of a small town.

Several situations of enhanced concentration of air ions with mobilities 0.32-0.5 cm²/(Vs) (diameter 1.4-1.9 nm) were recorded during long-time continuous measurements in Tahkuse, Estonia (Tammet et al., 1992). The extreme examples of hourly averages are:

	Date			Hour	Polarity	$0.32-0.5 \text{ cm}^2/(V \cdot s)$	0.5-2.5 cm ² /(V·s)
13	June	1985	3	a.m.	+	390	610
13	June	1985	3	a.m.	-	15	300
5	Sep	1985	5	p.m.	+	39	390
5	Sep	1985	5	p.m.		510	700

Concentration of ions with mobility

The well-developed charge asymmetry in the examples can be considered as a symptom of ion-induced nucleation on the cluster ions of one sign. Similar effects were measured in laboratory experiments before (e.g. B. A. Thomson and Iribarne, 1977). The annual average of the 0.32-0.5 cm²/(V·s) ion concentration in Tahkuse was 24 cm⁻³ as for positive as for negative ions. The time variations of partial concentrations of subfractions 0.32-0.4 and 0.4-0.5 cm²/(V·s) were intercorrelated positively as well as the partial concentrations of fractions with mobilities both over 0.5 cm²/(V·s). The concentrations of fractions one below and another over 0.5 cm²/(V·s) were not correlated. This observation is confirming the thesis that the mobility 0.5 cm²/(V·s) and diameter 1.3-1.4 nm can be considered as a border discriminating ultrafine particles from clusters.

The source of ions with mobilities $0.32-0.5 \text{ cm}^2/(Vs)$ in Tahkuse was not identified. The instrumentation was situated near a small farm where local sources of organic vapors were not controlled. The three-week measurements near the coastline in the area of Matsalu nature preserve in 1992 have shown, that the concentration of ultrafine aerosol ions with mobility $0.1-0.5 \text{ cm}^2/(Vs)$ typically does not exceed few ions per cm³ when local agricultural and biological sources of organic vapors are excluded. Probably, the ion-induced nucleation in the ground-level atmospheric air should be considered as essentially depending on the trace gases of biological and anthropogenic origin.

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A Particle Mass Spectrometer (PMS) Applied to Chemically Formed Particles

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1 Introduction

For the size analysis of particles suspended in liquids or gases numerous well tested measurement techniques are known. The difficulties in performing reliable and reproducible measurements increase with decreasing particle size, see [1-10]. In some applications it is interesting to detect and characterize ultrafine particles in the size range below 10 nm. These are from the technical point of view very small in terms of geometric dimensions but amount to an atomic scaling of more than 10⁵ amu (e.g. in the case of soot particles).

In the present paper a newly developed particle mass spectrometer (PMS) is described, which allows determination of the mass of charged ultrafine particles or large molecules. It combines different physical principles: a molecular beam technique to generate a particle beam, an electrical deflection and filter system which classifies the particles due to their kinetic energy and velocity in the beam, and a detection system for the charged particles. From all three, the probability density distribution of $m_P/z.e$ (i.e. the paticle mass per number of charges) can directly be determined.



Fig.1: Deflection of charged particles in an electrical field and resulting particle trajectories in a vacuum containment.





2 Summary of the PMS Principles

The basic principles of the particle mass spectrometer are described in [11] and should be summarized here again. According to Fig. 1, a particle beam characterized by the mass m_P (distributed property), the uniform velocity $\dot{x}_P = v_P$, and the electrical charge z e enters an electrical field in a capacitor of length l_K and width b_K . The field strength is $E = U_K/b_K$. An individual charged particle entering the electrical field is deflected by a force $F_y = z e U_K/b_K$ which has the direction of the field lines. It causes an acceleration of the particle in the y-direction according to its mass: $\ddot{y}_P = z e U_K/b_K m_P$. It can be assumed that gravity does not significantly influence the particle movement, e.a. $\ddot{x} = 0$. The individual particle trajectory and the velocity components inside the capacitor $0 \le x_p \le l_k$ or $0 \le t \le l_k/v_p$ can be described in cartesian cordinates using the time t as parameter:

$$y_P = \frac{1}{2} \frac{z e U_K}{m_P b_K} t^2 \qquad \qquad x_P = v_P t \qquad (1)$$
$$\dot{y}_P = \frac{z e U_K}{m_P b_K} t \qquad \qquad \dot{x}_P = v_P$$

Outside the electrical field the particles move along straight lines as indicated in Fig.1. The direction of the movement with respect to the x-axis results from the condition of constant velocity components \dot{y}_P and \dot{x}_P outside the capacitor. The particle trajectory is given by:

$$y_P = \frac{z e U_K}{m_P v_P^2} \frac{l_K}{b_K} \left(x_P - \frac{l_K}{2} \right)$$
for $x_P \ge l_K$.
$$(2)$$

Every individual particle of mass m_P and charge $z \ e$ has, according to Equ.(2), its individual trajectory $y_P = f(x_P)$; in other words: the originally uniform and well focused particle beam is now split up into a fan-shaped form. A grounded slit is now introduced, which is located at a distance x = l from the origin of the coordinate system having a slit width Δd at a position y = d from the x-axis. It separates a certain class of particles which can pass the slit whereas the rest is blocked and collected by the grounded plate. From re-arranging Equ.(2) introducing $y_P = d$ and $x_P = l$ the kinetic energy selecting operation of the whole arrangement will become obvious.

$$\frac{m_P}{z e} \frac{v_P^2}{2} = U_K \frac{l_K}{b_K} \left(\frac{2l}{d} - \frac{l_K}{d}\right)$$
(3)

For fixed geometrical conditions, the voltage U_K selects particles of the kinetic energy $m_P v_P^2/2$ carrying z elementary charges. In other words: U_K is a direct measure of the kinetic energy of such particles which can pass the slit arrangement.

$$U_K = const \ \frac{m_P}{ze} \ \frac{v_P^2}{2} \tag{4}$$

The proportionality between particle mass $m_P/z \ e$ and the deflection voltage U_K can according to Equ. (4) be obtained, if the particle velocity v_P is known. This property can be measured by an electrical chopping system, which is illustrated in Fig. 2. The selected beam of charged particles passes through two grids supplied with a synchronously pulsed repelling potential. The upper grid forms packages of charged particles, whereby the package length l_P depends on the frequency of the grid voltage f and on the particle velocity v_P . Whether the full package of particles or only part of it can pass the second grid and reach the monochromator slit can be estimated by a simple geometrical phase condition. Only very few or no particles pass the second grid if the package length l_P is an odd-numbered multiple of the grid distance l_G . This results in a series of minima of the electrical current I or the particle flux I_P at frequencies $f_{min,i}$ for the following conditions:

$$v_p = 2 f_{min,i} l_{p_i}$$

 $l_{p_i} = l_G, l_G/3, l_G/5, el$

(5)

For the determination of the particle velocity v_P , the frequencies $f_{min,i}$ of the repelling potential must be determined which cause a minimum of the particle flux I_P . This minimum frequency respectively the particle velocity v_P can be measured for every group of particles selected by the deflection voltage U_K . So Equ. (4) can be further simplified to its final form:

$$U_K = const \frac{m_P}{z e} \tag{6}$$

The remaining problem of the PMS is to determine the particle flux classified by both the deflection voltage U_K and the monochromator slit. The simplest way is to collect the charged particles by a Faraday cup and to convert it into an equivalent electrical current I by a very sensitive electrometric amplifier. This was done in the present case, see chapter 4. The measured electrical current I is, e.g. for singly charged particles (z = 1), directly proportional to the particle flux passing the slit

$$I = f(U_K) \sim \Delta \dot{N}_P \tag{7}$$

For particles carrying more than one elementary charge (z > 1) the situation is principally similar.

3 Realization of the PMS

To realize the measurement principles of the PMS it is necessary to transfer the particles of a normal aerosol into a beam of particles moving inside a vacuum containement. This is possible by applying the molecular beam technique, which is well known from classical gasdynamics. The general situation is schematically illustrated in Fig.3. We assume that the ultrafine particles of the aerosol were partly charged





Realization of the PMS: generation of a particle beam by differential pumping. @aerosol inlet, @aerosol chamber with nozzle, @intermediate vacuum chamber with skimmer, @ high vacuum chamber with capacitor, @Faraday cup, Camplifier.





Particle kinetic energy and particle velocity analysers: (a) capacitor, (b) electrically grounded blend with slits, (c) grid, (d) electrometric amplifiers, (e) Faraday cups. by either the particle generation process itself or by an appropriate charge source. A probe of the aerosol is supersonically expanded through a 0.7 mm platin plated and electrically grounded 45° quarz nozzle into a vacuum chamber. The pressure is kept to a level of about 10^{-3} mbar by two oil diffusion pumps (2 \times 1000 l s⁻¹) with cooled baffles connected to a conventional rotary pump. The supersonic free jet formed by the nozzle expansion flow contains both particles and molecules. The flow conditions are such that the gas temperature decreases very rapidly freezing any physical or chemical rate process inside the expanding aerosol probe nearly completely. Also the gas density decreases by several orders of magnitude. With increasing axial coordinate, the flow changes to free molecular conditions. The centre of the free jet is extracted by a skimmer and moves as a particle or molecular beam into a second vacuum chamber. The pressure is maintained constant at a value of 10^{-5} mbar by a turbomolecular and a rotary pump. The skimmer, which has an opening diameter of about 0.65 mm, is located 75 mm downstream of the nozzle orifice. This long distance causes a low density at the skimming position in the free supersonic jet but results in a small divergence of less than 0.5° of the particle beam.

The two devices used to classify the particles due to their kinetic energy as well as to determine the velocity of the classified charged particles are illustrated in Fig.4. The capacitor used for the kinetic energy selection is located 80 mm downstream from the skimmer entrance and consists of two flat copper electrodes of length $l_k = 60$ mm length and 30 mm width having a distance of $b_k = 16.3$ mm. A resistor network ensures that the applied voltage -200 V $\leq U_k \leq +200$ V is symmetrical to the grounded potential. The electrical field between the two copper electrodes seperates the charged particles according to their polarity and splits the well focussed beam into a fan of charged particles such that particles having a small value of m_p/ze show a stronger deflection from the undisturbed beam direction than the larger ones. The classification of the particles due to their kinetic energy was performed by introdu-



Fig.5: Modified analyser for cumulative detection of charged particles. (a) capacitor, (b) grounded blend, (c) grid, (a) amplifier, (c) electrode



Fig.6: Examples of measured PMS spectrum (upper part) and measured particle velocity (lower part).

cing a grounded plate (b) into the fan-shaped beam of charged particles carrying two symmetrical slits of $\Delta d = 5$ mm width at a distance of 2d = 90 mm. The distance between the capacitor entrance and the slit plate is l = 240 mm. The fraction of charged particles being able to pass through the slits were collected by the two Faraday cups (c), to which they deliver their electrical charge. Two ultra-sensitive amplifiers (d), which are able to measure currents in the fA range, transform the particle flux ΔN_P into an equivalent electrical current I with a signal-to-noise ratio larger than 100.

The setup illustrated on the left hand side of Fig. 4 allows us to determine the velocity of the charged particles in the beam. It consists of two grids having a distance of $l_G = 150 \ mm$. They were supplied with a pulsed voltage of variable frequency working as repelling potentials. To limit their spatial influence both were covered with grounded grids, not shown in Fig. 4. By tuning the pulse frequency, this device operates as a velocity filter. The resulting currents plotted as a function of pulse frequency show distinct maxima and minima, which can be related to the particle velocity, see chapter 4.

A modified device, which was also used during some of the PMS test measurements is shown in Fig. 5. It employs a small central point electrode for collecting the charged particles. By tuning the deflection voltage U_K from 0 to +5.000 V or from 0 to -5.000 V the resulting decreasing electrical currents represent the integrated particle flux in the respective particle mass range. This setup was used to measure the cumulative mass or energy spectra of relatively heavy particles.

4 Examples of Measured Particle Energy and Mass Spectra

The particle mass spectrometer was tested by applying it to ultrafine aerosols generated in sooting flames burning from top to bottom inside chamber (b) of Fig. 3.

The flames used to produce carbonaceous particles of different size and structure were stabilized at low pressure on an 75 mm diameter water cooled sintered bronze plate. The pressure in the combustion chamber was held between 20 mbar and 30 mbar by mechanical vacuum pumps. Fuel (C_2H_2) and oxidizer (O_2) were premixed by calibrated flow meters and supplied to the burner head. In the experiments the C/O ratio was varied between 1.0 and 1.3, and the velocity of the cold unburned gas ranged between 45 $cm/s \le v_u \le 60 cm/s$. The whole burner can be moved in the vertical direction to vary the distance between burner plate and the fixed nozzle $(0 \ mm \le HaB \le 160 \ mm, HaB = height above burner)$. In this way probes can be taken from different positions in the flame containing particles of different chemical age. The formation of carbonaceous particles in sooting flames is a complicated process, which is not completely understood. Homogeneous and heterogeneous chemical reactions contribute to the formation of high molecular weight hydrocarbon mulecules, soot precursers, and to the surface growth of soot particles. Additionally, particle coagulation is always present in such systems. In slightly sooting flames of the present type also different sorts of fullerenes were found. It is important to notice that a considerable amount of particles and molecules are electrically charged as a result of the high temperature flame processes.

An example of directly measured particle properties is shown in Fig. 6. Probes containing charged soot particles were taken from the low pressure burner at a height of HaB = 60 mm. C_2H_2 and O_2 were burning at p = 25 mbar with a C/O mixing ratio of 1.1. The upper part of Fig. 6 shows the measured Faraday cup current as a function of the deflection voltage U_K both for positively and negatively charged particles. The signal to noise ratio of the measurement is excellent. Both curves have three maxima at voltages $U_K = 30V$, 60V and about 120 V. The highest middle peak lies at twice the voltage of the first peak. From the overall particle formation history not discussed here in detail and from the exact ratio of 2 between the peak positions, it can be concluded that the peak at $U_K = 60V$ must be related to singly charged particles whereas the peak at $U_K = 30V$ indicates particles of the same kinetic energy or mass class carrying two elementary electrical charges. According to Equ.(4) the deflection voltage U_K can be related to the particle kinetic energy. For z = 1 a voltage of $U_K = 60V$ results in an energy value of $m_p v_p^2/2 = 7.85 \cdot 10^{-17} J$.

The particle velocity measurement illustrated in the lower part of Fig. 6 was performed on positively charged particles being deflected by voltages $U_K = 60V$ and $U_K = 30V$ corresponding to the maxima in the upper part of Fig. 6. The measured currents as a function of the filter frequency show two minima at $f_{min,1} = 3.3 \ kHz$ and $f_{min,2} = 9.6 \ kHz$. According to Equ. (5) the current minima result in a mean particle velocity of the selected energy class of $v_p = 960 \ m \ s^{-1}$. In further experiments the velocity of other particles belonging to other energy classes selected by the deflection voltage U_K was also measured. The results not shown here, allow to transform the deflection voltage scale of Fig. 6 into a particle mass scale as indicated there. The particles selected by the deflection voltage $U_K = 60V$ have a mass of $m_p = 1.7 \cdot 10^{-19}g$ or in corresponding atomic mass units $m_P = 101.800 \ amu$. It is important to note that a calibration of the PMS is not necessary, which is an advantage of this measurement principle. It is common practice in aerosol science to characterize nm-particles by their size. This requires in the present case the assumption of a particle material density. An often used value for soot is $\rho = 1.8 \ g \ cm^{-3}$,







Fig.8: Probability density functions of the particle mass obtained from the mass spectra in Figs. 6 and 7.

which converts the given particle mass to a mean size value of $d_p = 5.65 nm$.

Another example of measured carbonaceous particles, which demonstrate the low mass side of the PMS is shown in Fig. 7. In this case probes were taken from a visibly non-sooting flame (C/O = 0.95) at two subsequent positions HaB = 20 mm and $HaB = 30 \ mm$. The energy spectra of positively and negatively charged species show again a multi-peak structure. The deflection voltage U_K is considerably lower than in the example of Fig. 6 and also the measured electrical current is reduced by a factor of about 50. Both facts indicate very light charged species with significantly reduced number concentration at the probing position in the flame. By comparing both mass spectra of Fig. 7 it is obvious that the main peaks are shifted to the right with increasing HaB indicating a mass growth of the particles with increasing time. It is a remarkable fact that the mass peak of negatively charged species appearing at a deflection voltage of $U_K = 2 V$ remains at this position. Contrary to the other particles a considerable amount of these negative ions are not willing to grow. A velocity measurement yielded a value of $v_p \approx 1500 \ ms^{-1}$, which is above the velocity of the heavier particles. Assuming single charged particles (z = 1)the deflection voltage axis of Fig. 7 can be converted into the given mass axis in atomic units (amu). The current signal at $U_K \ge 1 V$ correlates with a mass of $m_P \geq 750 \ amu$, which is in the range of big molecules. We believe that this mass peak indicates fullerenes, which were detected by time-of-flight mass spectroscopy in very similar C_2H_2/O_2 flames.

5 Sensitivity and Resolution of the PMS

The energy or mass spectra of Figs. 6 and 7 look on the first view equal to probability density functions of the particle kinetic energy or the particle mass. This is not true

because the sensitivity of the PMS depends on the deflection voltage U_K . This can be shown by the following analysis: according to Fig. 1, the flux of charged particles \dot{N}_P entering the electric field is split into a fan-shaped beam resulting in a y-distributed particle flux P(y) in a plane at x = const. The total flux is:

$$\dot{N}_P = \int_0^\infty P(y) \, dy \tag{8}$$

On the other hand the total flux of charged particles can also be related to the energy distribution of the particles in the beam.

$$\dot{N}_P = \int_0^\infty Q(E) \, dE, \tag{9}$$

with $E = m_P v_p^2/2$. The quantity Q(E) is the required probability density function (PDF) of the particle kinetic energy or respectively for $v_p^2 = const$, the PDF of the particle mass. The relation between Q(E) and P(y) is:

$$Q(E) = P(y) \frac{dy}{dE}$$
(10)

The PMS-Equs. (3), (4) yields for a fixed deflection voltage U_K and $y \equiv d$ the relation between dy and dE:

$$\frac{dE}{E} = -\frac{dy}{y} \tag{11}$$

The combination of Eqs. (10), (11) and (4) results after discretization in:

$$Q(E) = -P(y) \Delta y \frac{y}{U_K \Delta y} const$$
(12)

The final step in this analysis is to introduce the measured electrical current I. It must be equal to the number of particles passing through the slit times the number of charges per particle. For particles carrying only one electrical charge (z = 1), the current I is:

$$I = \Delta N_P = P(y) \,\Delta y \tag{13}$$

The combination of Equs. (13) and (12) reveals the relation between measured electrical current and PDF for the particle kinetic energy or mass. Furthermore, the constant geometrical conditions y = d (slit position) and $\Delta y = \Delta d$ (slit width) were introduced and summarized together with the other invariant properties to a further constant factor.

$$Q(E) = const \frac{I}{U_{K}}$$
(14)

This final equation indicates that not the electrical current but the current divided by the energy-proportional deflection voltage U_K is equal to the probability density function. Fig. 8 shows two examples of the earlier discussed energy spectra converted via Equ. (14) to PDF of the particle mass. Compared to the mass spectra, the different mass peaks are slightly shifted to smaller mass values and the relative peaks heights at small mass units were increased.

From conventional mass spectroscopy, the resolution R is known to be introduced by: $R = m/\Delta m$. In this expression m is the selected mass and Δm the width of the recorded mass peak, which can e. g. be determined at 10% peak height. In this case the ions selected by the PMS have a fixed mass value so that the width of the mass peak is a real measure of the resolution. In the present case of the PMS, the situation is more complicated because the peak width in the spectrum is influenced by both the PMS resolution and the distribution of the particle mass. For the following short analysis, we assume that all particles of the selected mass class have a uniform velocity, and that the number of charges per particle is known. We define the PMS resolution analog to the conventional mass spectroscopy:

$$R = \frac{m_P}{\Delta m_P} \tag{15}$$

The PMS-Equs. (3), (4) can be re-arranged under the above assumptions resulting in the modified form:

$$m_P = const \, \frac{U_K}{d} \tag{16}$$

The differentiation at constant U_K and the change from differentials to differences yields an equation similar to Equ. (11), which relates the mass width Δm to the slit width Δd of the PMS.

$$\frac{\Delta m_P}{m_P} = -\frac{\Delta d}{d} \tag{17}$$

$$R = \left| -\frac{d}{d} \right| \tag{18}$$

Equ. (18) is the final equation for the PMS resolution. As can be seen,
$$R$$
 depends
only on the geometrical PMS properties slit position d and slit width Δd and is
independent on the deflection voltage U_{K} .

 Δd

According to Equ. (18) several possibilities exist for improving the resolution of the PMS, see [11].
6 Conclusions

The newly developed particle mass spectrometer is a scientific instrument allowing to determine the mass of large molecules and ultrafine particles and agglomerates. The main advantages are:

- the PMS delivers the particle mass directly and in-situ and does not need calibration,
- the PMS mass determination is independent on the geometrical structure of the particles as well as on chemical or optical particle properties.

The present version of the PMS can be further improved by increasing the sensitivity and the resolution.

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