Characterisation of Nanoparticles Synthesized in the Microwave Plasma Discharge Process by Particle Mass Spectrometry and Transmission Electron Microscopy

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INTRODUCTION

The physical and chemical properties of nanoparticles frequently depend on their particle size distribution. Previous studies have shown that the microwave plasma (MWP) process yields non-agglomerated nanoparticles in the size range up to 30 nm (Vollath and Sickafus, 1992). The approximate size from bulk samples was determined by Transmission Electron Microscopy TEM. However the sampling and accurate picture analysis of these particles by TEM is very difficult due to their poor contrast and overlapping of particles. More recently Janzen et al. (2002) and Mätzing et al. (2003) reported the first full characterisation of various metaloxide nanoparticles from the MWP by particle mass spectrometer (PMS). These size distributions show modal values of 4 – 5 nm (ZnO, Fe_2O_3, SiO_2) and narrow geometric standard deviations. The comparison of PMS- and TEM-derived sizing information shows that the PMS is a reliable and efficient tool for the investigation of the MWP process. Here we report our results concerning the influence of precursor concentration and microwave power on the size distribution of iron oxide and silica nanoparticles produced by the MWP.

MICROWAVE PLASMA PROCESS

The MWP-process used in this study is shown in figure 1. Liquid iron pentacarbonyl (99,9 %) under helium pressure (2 bar) is metered by a mass flow controller (2-15 mg/min) into a heated evaporation chamber and mixed with Argon. The gas is diluted by a mixture of Ar/O_2 (4 - 10 slpm) and flows into a quartz-tube which is housed in a metal applicator for the microwave power (300 – 700 W). The microwave generator consists of magnetron ($P_{max.}$ = 850 W), isolator, directional couplers and wave guides. The nonthermal plasma is operated at T < 200 °C and a pressure of 10 to 50 mbar. The frequency of applied microwaves is 2.45 GHz. These experimental conditions lead to residence time of the nano particles in the plasma zone in the range of milliseconds. Upon addition of the precursor the burning plasma immediately exhibits a bright pink colour and particle formation occurs instantaneously.

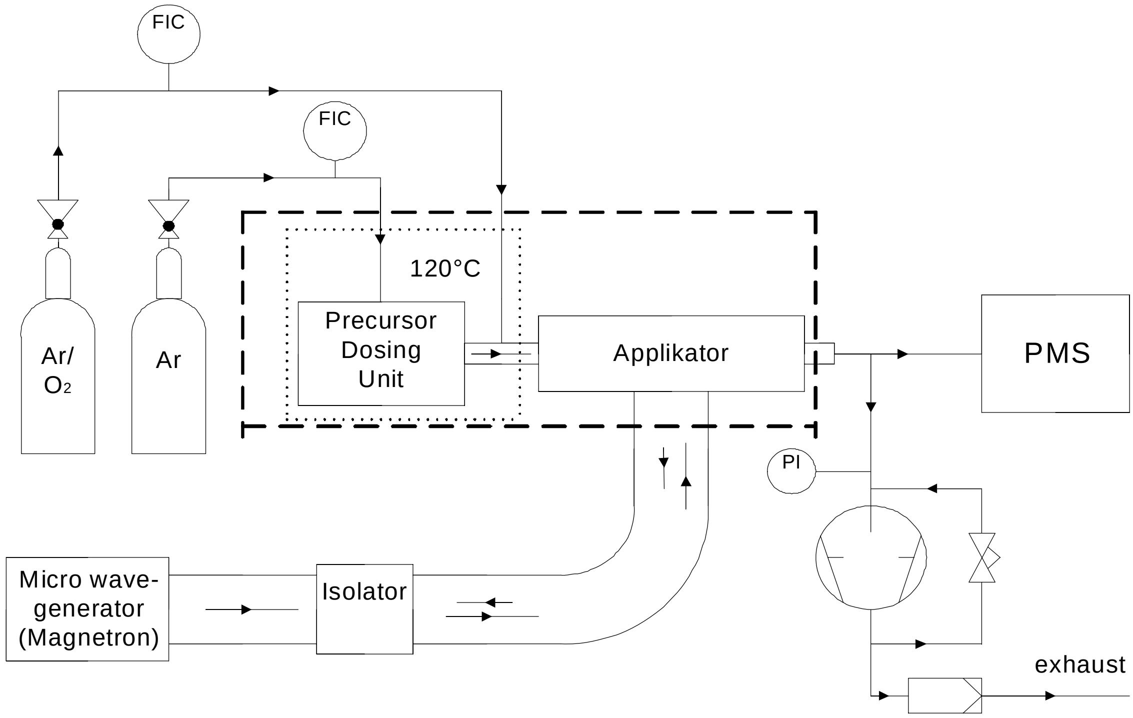


Figure 1: Flowsheet of the MWP-process for production of nanoparticles with attached PMS

PARTICLE MEASUREMENTS

The charged species of nanoparticles produced in microwave plasma enables to measure the size distribution by a novel Particle Mass Spectrometer (Paur et al., 2005). With this system it is possible to measure on-line the size distributions of charged nanoparticles in the range from 0.5 to 50 nm with high number concentrations c_N over 10^9 cm^{-3}. The gas borne particles are sampled from the quartz tube by a two stage molecular beam sampling system into the PMS detection chamber. In the first stage a super sonic expansion of the sample into a free-molecular regime leads to freezing of all gas-particle interactions. In the detection chamber of PMS the particle beam passes a deflection capacitor which separates the charged particles according to their polarity and deflects them according to the ratio of their kinetic energy to charge ($U \sim ½·m·v^2/z$). By variation of the deflection voltage particles of different energy-to-charge ratios reach the faraday cup which is located symmetrically at fixed off-axis positions at the end of the detection chamber. The current signal generated at the faraday cup is proportional to the incoming number of particles times their total charge. The results can be evaluated to give the ratio of mass to number of charges (m/z). To convert the energy spectrum into particle size distribution, the number of charges z, the particle speed v and the material density ρ must be known.

RESULTS AND DISCUSSION

The figure 2 shows the size distribution of iron oxide nanoparticles produced by the MWP-process as measured by the PMS and by the analysis of TEM micrographs.

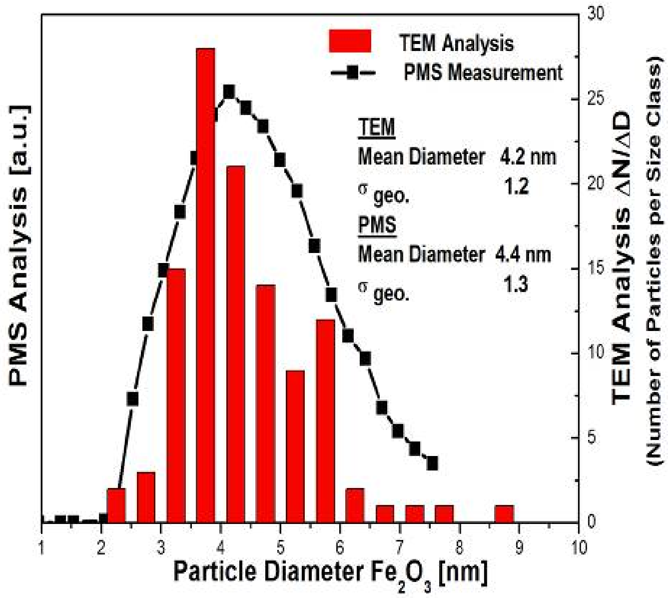
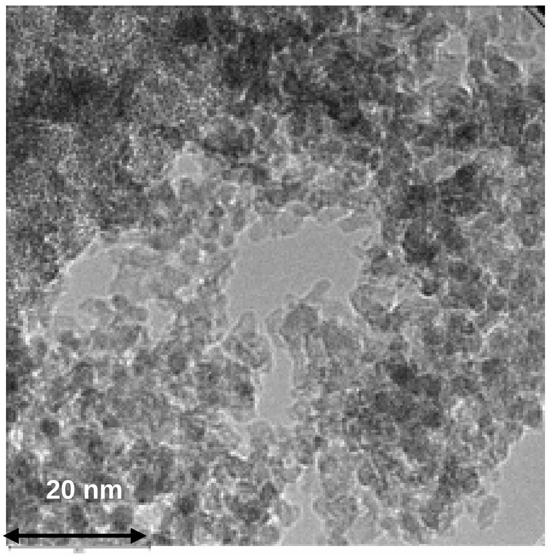


Figure 2: Size distribution of iron oxide nanoparticles by TEM and by PMS ($P_{Magnetron}$ = 340 W; $Fe(CO)_5$ = 280 ppm; p = 25 mbar)

In agreement with the spectra reported by Janzen et al. (2003) the mean particle diameter is about 4,5 nm with an extremely narrow width $\sigma_{geo.}$ of 1,3 nm. This result is also supported by the electron micrograph, which was obtained from a sample which has been deposited from the molecular beam of the PMS. Thus both methods – PMS and TEM - provide reasonable agreement of modal diameter and geometric standard deviation $\sigma_{geo.}$ of the size distribution.



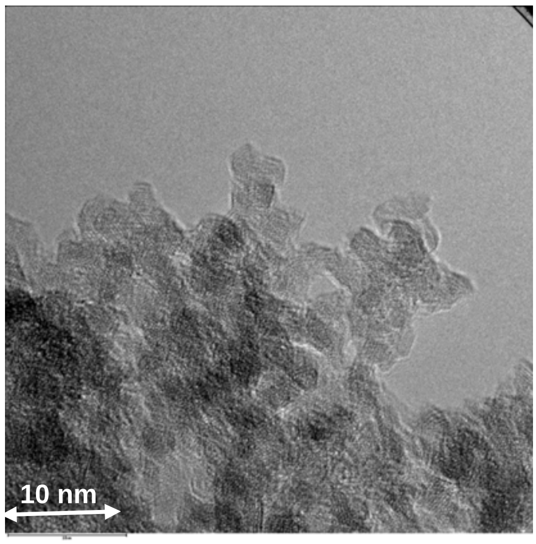


Figure 3: Micrographs of iron oxide nanoparticles synthesized in the MWP-generator (explained conditions as in Figure 2)

Figure 4 and 5 shows the influence of the $Fe(CO)_5$ concentration and the microwave power in the process. As expected the increase of the $Fe(CO)_5$ concentration leads to a larger modal particle diameter and the microwave power hasn`t any influence on the particle diameter but a strong one on the number concentration.

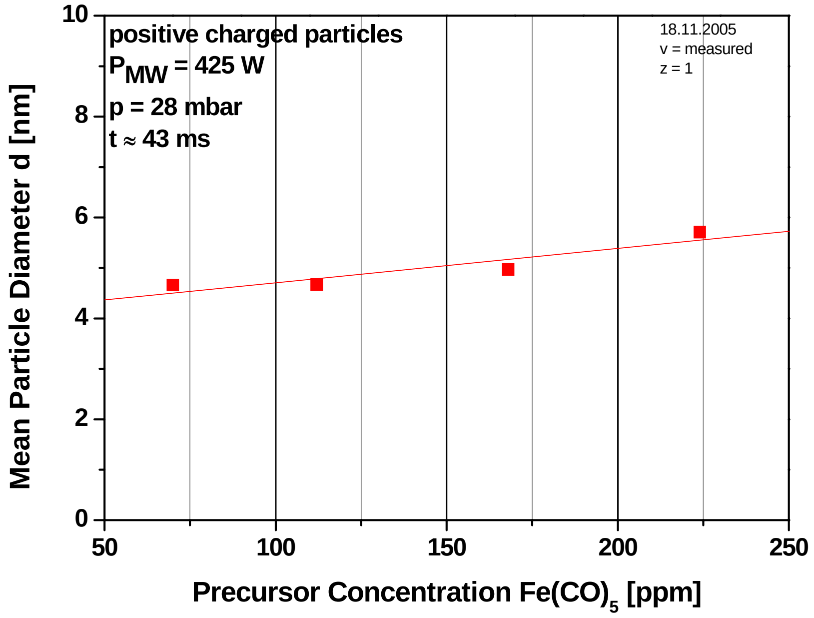


Figure 4: Dependence of mean particle diameter on the precursor concentration in the MWP-synthesis of Fe_2O_3-nanoparticles

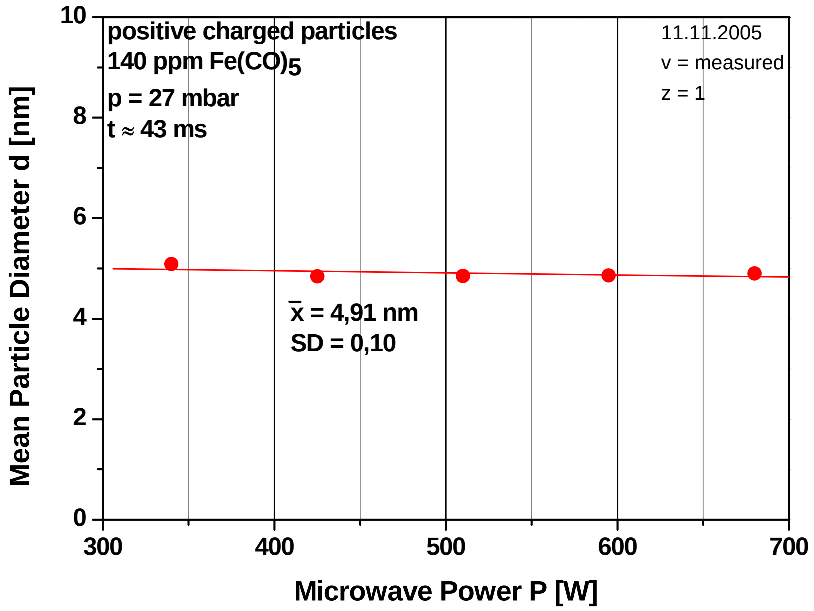


Figure 5: Dependence of mean particle diameter on the microwave power in the MWP-synthesis of Fe_2O_3-nanoparticles

CONCLUSIONS

The size distributions of iron oxide nanoparticles produced by the MWP-plasma process were measured by PMS and TEM. Both methods provide reasonable agreement of the modal diameter and geometric standard deviation of the size distribution. By variation of the precursor concentration the particle diameters are changed in the range between 4.5 up to 5.5 nm. With respect to the industrial application of the process more data are required to determine the sensitivity of the MWP-process to variations of the technological parameters.

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Keywords

Nanoparticle, microwave plasma discharge, particle mass spectrometer, transmission electron microscope

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