

SYNTHESIS OF COATED NANOPARTICULATE CERAMIC POWDERS

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ABSTRACT

The microwave plasma process is capable to produce larger quantities of nanoparticulate powders with mean particle sizes in the range from 5 to 20 nm. The products may be oxides, nitrides, sulphides, selenides, or even metals. Additional, it is possible to coat these particles with a layer of a second ceramic, a polymer or carbon. Sintered $ZrO_2-Al_2O_3$ nanocomposites and superparamagnetic cores of $\gamma-Fe_2O_3$ -polymer composites are given as examples.

INTRODUCTION

Considering their special properties the application of nanoparticulate ceramic powders is increasing. In most cases, these are the properties of isolated particles of a certain size. For technical applications macroscopic bodies or other arrangements of many particles are a prerequisite. Therefore, two major problems thwart a broad application of these materials:

- Interaction of the nanoparticles.

This is a major problem, in special for magnetic or optical applications.

- Thermal grain growth.

This problem is arises during sintering or any application of nanomaterials at elevated temperatures.

Coated nanoparticles solve these problems. These are nanoparticles with sizes in the range from 5 to 20 nm with a coating of a second ceramic phase or a polymer. The thickness of this coating is also in the range of a few nanometers. The interaction of the nanoparticles in question determines the necessary thickness of the coating. It is certainly different in systems, where tunneling has to be avoided as compared to those with long range acting fields such as magnetic dipole fields. Besides of this background, based on the physical interaction and thermal stability for coated nanoparticles, one has a further group of reasons for particle coating: Coating makes it possible to have particles with a certain set of physical properties in the kernel and a second tailored set of chemical properties at the surface. A typical example for this case are carbon coated silica particles.

There are two strategies possible to select the coating of nanoparticles:

- Ceramic nanoparticles with ceramic coating. A necessary prerequisite for successful coating is that kernel and coating have no mutual solubility in the temperature regime of synthesis, sintering, and application. For a few very special applications a stability for the time of synthesis is sufficient.
- Nanoparticles with polymer coating. This type of coating is possible, if the polymer does not dissociate catalytically at the surface of the particle. The main application of this type of coated particles is in systems, with applications at ambient temperature.

Coated nanoparticles are synthesised by the microwave plasma process. [1,2] Ceramic coatings are obtained by cascading different microwave plasma reaction zones consecutively on one reaction tube. [3,4] Polymer coating is performed directly after a reaction zone outside the plasma region. [5]

SYNTHESIS

Chemical reactions, thwarted under normal conditions by kinetics or thermodynamics, can be used to synthesise nanophased ceramic powders in a microwave plasma. This is due to a partly dissociation and ionisation of the reactants in a plasma. The existence of ionised and dissociated species in the plasma enhances the kinetics of the chemical reactions. In a microwave plasma, the energy transferred to a charged particle by an oscillating electric field is inversely proportional to the mass of the particle and the squared frequency. Additionally, collisions between energy rich charged particles and uncharged ones influence the energy transfer resulting in a significant influence of the gas pressure to the energy transfer. As the mass of the electrons is significantly smaller than the mass of the ions at high frequencies the transfer of energy is substantially higher to the electrons than to the ions. The neutral species obtain their energy from collisions with the charged ones. Therefore, the "overall temperature" of a gas passing a microwave plasma is not as high as in a dc or rf plasma. Depending on the gas pressure and the input of microwave energy the temperature determined directly after the plasma zone can be adjusted in a range from 150 to 800°C. Adjusting the reaction temperature to such low values avoids the formation of hard agglomerates in the nanopowders.

Experimentally, ceramic nanopowders are synthesised of in a 50 mm diameter reaction vessel made of quartz, passing a single mode TE_{11} rotating mode cavity. [6] This cavity is connected to a 0.915 GHz microwave system using a IEC 153 R9 (equivalent to RETMA WR 975) waveguide. The total system is tuned using a tri-stub tuner. An equivalent design for 2.45 GHz is also operated successfully. For large scale applications the diameter of the reaction tube may be increased up to a diameter of about 180 mm. The TE_{11} rotating mode design does not need a sliding short for tuning. Additionally, a TE_{11} rotating mode cavity has no geometrical limitations by the wave guide. This makes it possible to adjust the length of the cavity to the needs of the process. Figure 1 shows this set-up.

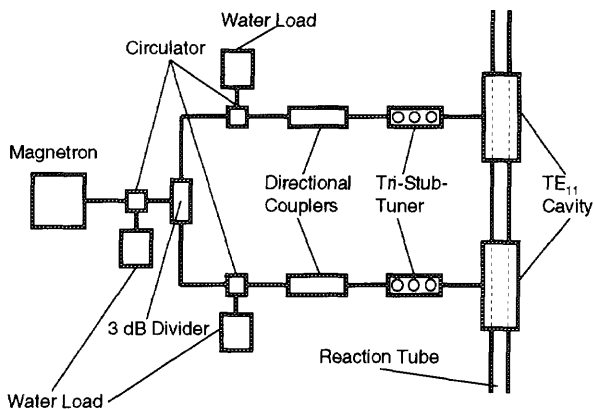


Figure 1: Set-up of the microwave system for the synthesis of coated ceramic nanoparticles.

The major advantage of this design over the standard TE_{01} design is the increased efficiency in the use of the microwave power. Figures 2 exhibits the microwave efficiency of the plasma loaded cavities as a function of the gas pressure and the tuning. This shows that the region of efficient operation is relatively broad. Optimising tuning, e.g. for 40 mbar one has good operating conditions in the range from 10 to 70 mbar.

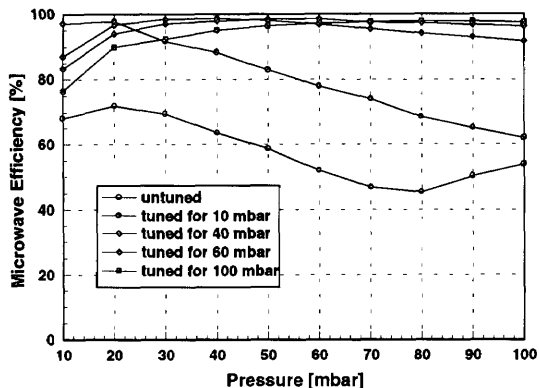


Figure 2: Microwave efficiency for a plasma loaded TE₁₁ microwave reaction cavity. The tuning of the cavity was optimised for different gas pressures-

Depending on the mixtures of reaction gases it is possible to synthesise oxides, nitrides, sulphides, selenides, and in special cases metals and carbides. Precursors are chlorides, carbonyls, metallocenes, or organometallics. The precursors are evaporated and introduced into the reaction tube directly in front of the plasma zone where the particles are formed. The particles formed in the plasma zone carry electrical charges. This prevents the collision of the nanoparticles and reduces the probability of cluster formation. The reaction temperature, i.e. the temperature measured directly after the reaction zone can be adjusted in the range from 150 to 800°C. The low temperatures are of special importance, because low temperatures reduce the probability of the formation of sintered clusters. The residence time of the particles in the reaction zone is less than 10 ms. Reaction rate and residence time are parameters to adjust the particle size within relatively narrow limits. The mean diameter of the smallest particles that can be produced with a reasonable production rate is about 3 nm. The largest mean particle diameter is in the range of about 20 nm. To produce larger particles it is necessary to change the reaction route. In the case of oxides the addition small quantities of water to the reaction gas leads to larger particles. [1]

Particles coated with a ceramic layer are produced in a system with two reaction zones as it is depicted in Figure 1. In this case the two different precursors are introduced into the system directly in front of each reaction zone. [3,4] To obtain a polymer coating an appropriate monomer is evaporated and introduced into the reaction tube directly after the reaction zone. Now the molecules of the monomer condense on the surface of the nanoparticles. This condensate polymerises under the influence of temperature and the UV-radiation, emitted by the microwave plasma. [5] Finally, the product is collected on cooled surfaces and scrapped off.

CHARACTERISTICS OF THE PRODUCT

The particle size of the powder is, for crystallised material, in most cases in the range from 5 to 10 nm. High resolution electron microscopy is the main tool for characterisation. As an example for the special physical properties of nanomaterials, the magnetic behaviour is described.

Ceramic Coated Nanoparticles

It is a necessary prerequisite for successful coating that kernel and coating have no mutual solubility. There is a sufficient number of important ceramic systems fulfilling this condition. Figure 3 shows three zirconia particles coated with alumina. Two of these particles are oriented in a way that lattice fringes are visible. The essential point is that two of these three particles are iso-

lated ones; one is an agglomerate consisting of two particles. This micrograph shows that the formation of agglomerated particles is a very special occurrence. Additionally, it is obvious that there is no interdiffusion between zirconia and alumina.

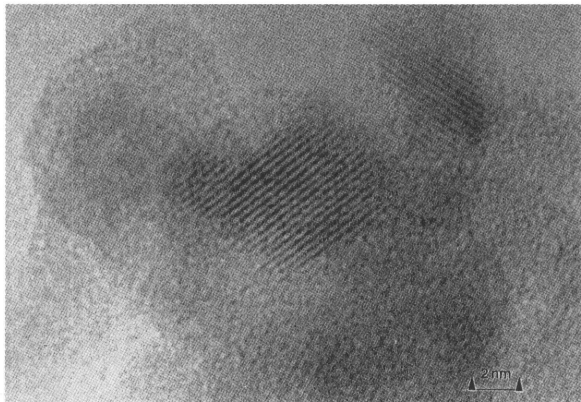


Figure 3: Crystallised zirconia (ZrO_2) particles coated with glassy alumina (Al_2O_3). There is no interdiffusion zone between the two phases.

Pressing and sintering of a powder as it is shown in figure 3 leads to the structure depicted in figure 4. During sintering the alumina coating acts as a diffusion barrier. This avoids dissolution of the small zirconia particles in the matrix and suppresses grain growth in the zirconia phase during sintering. Figure 4 shows an electron micrograph of such a sintered specimen. Strain or absorption contrast caused by some interdiffusion may be the reason for the shadow around the particles.

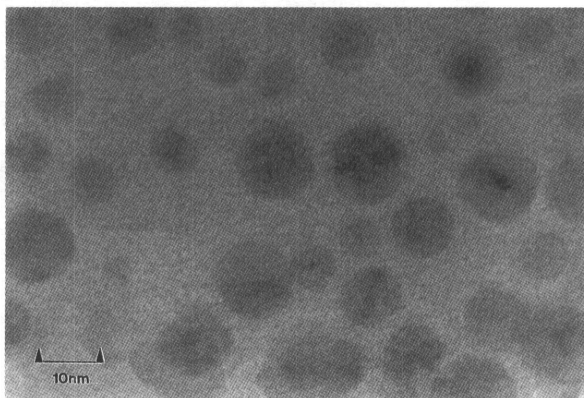


Figure 4: Sintered zirconia (ZrO_2) particles coated with glassy alumina (Al_2O_3). The shadow around the particles may be due to strain contrast or interdiffusion.

Polymer Coated Nanoparticles

The process to coat ceramic nanoparticles with a polymer is similar to the one described above. [5] The particles produced in the first step act as condensation seeds for an evaporated monomer provided temperatures are selected properly. In this case the monomer will condense on the surface of the particles and polymerise under the influence of temperature and UV-radiation from the plasma. During this process, the particles lose their electrical charges. Therefore, a significant amount of the polymer coated particles will agglomerate. Figure 5 depicts the

resulting product. Coating of transition metal oxide particles is sometimes extremely difficult because of the catalytic properties of these extreme high surface particles. Careful selection of the conditions for coating can avoid this problem.

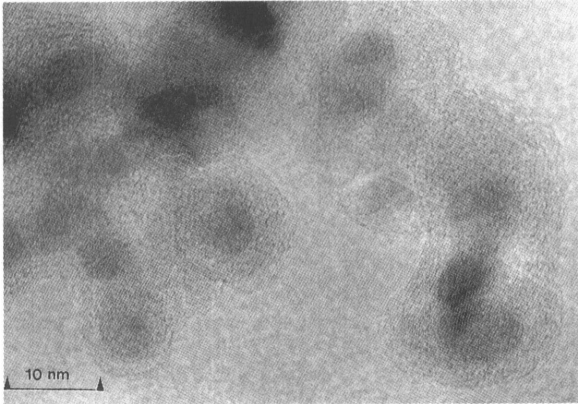


Figure 5: Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles coated with poly-methacrylic-acid (PMA).

A typical application of polymer coated ceramic nanoparticles are soft magnetic cores. Superparamagnetic particles are free of any magnetic hysteresis. [7,8] This is valid up to frequencies in the range of one Gigahertz. Superparamagnetism is a property of isolated small particles of ferri-magnetic materials. To produce a magnetic core of superparamagnetic particles, the superparamagnetic particles have to be kept on distance to reduce their interaction. Figure 6 shows typical magnetisation curves of small cylinders made of such materials. These specimens were consolidated with hot pressing at 100 °C. This material is perfect for this application.

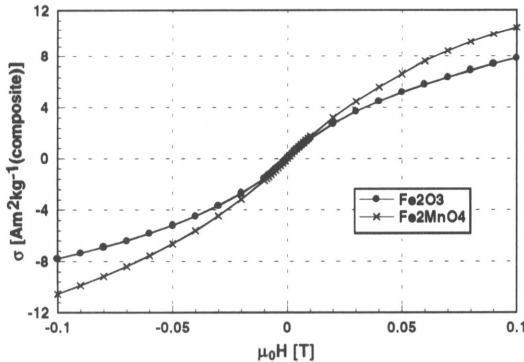


Figure 6: Magnetisation curves of superparamagnetic Fe_2O_3 and Fe_2MnO_4 -PMA composite cylinders (ca. 3 mm \varnothing , 4 mm high) at 300 K.

In this figure one realises magnetisation curves that are obviously free of any hysteresis. Because of a significant polymer content the magnetisation of this material is smaller than the one obtained with pure ceramic ferrite.

Using polymer coated ferrite particles it is possible to produce magnetic core simply by hot pressing at 100 °C. This is cheaper than the standard fabrication process consisting of cold pressing and high temperature sintering.

Carbon Coated Oxide Particles - Oxide Coated Carbon Particles

The synthesis of these materials has to be performed in the plasma zone. [9] Under the conditions of the plasma any system oxide - carbon is far away from equilibrium. Improperly selected processing conditions lead to immediately oxidation of the carbon; a coating is not formed. Experimental conditions leading to a useful result excel in extreme short residence time of the particles in the coating zone. A typical example is the system SiO_2 core coated with carbon. Under the conditions of the microwave plasma synthesis, one obtains glassy silica particles with sizes in the range from 10 to 20 nm. The carbon coating is amorphous.

CONCLUSIONS

The microwave plasma process is capable to produce larger quantities of nanoparticulate powders with mean particle sizes in the range from 5 to 20 nm. From the broad spectrum of possible products some applications in the field of nanoscaled oxide particles have been demonstrated. Because of the dissociation and ionisation the reactants in the plasma, the microwave plasma process excels in relatively low reaction temperatures. The low reaction temperature and the electrical charging of the particles in the plasma reduce the probability of agglomeration. Therefore, it is possible to pass the gas stream with the as produced particles through a second reaction zone to coat the particles. The thickness of a ceramic coating can be adjusted up to 5 nm.

Non-equilibrium combinations such as polymer coated oxide particles and carbon coated silica are also possible. Coating particles with a polymer layer is performed by condensing an appropriate monomer on to the surface of the particle and subsequent polymerisation with the UV-light from the plasma. The selection of the monomer is very critical, because many oxides, in special the oxides of the transition metals act as a catalyst and decompose the monomer on the particle surface. The thickness of this polymer coating is in the range from 5 to 15 nm.

To prove the concept of coated particles the structure of a sintered $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and the superparamagnetic behaviour of $\gamma\text{-Fe}_2\text{O}_3$ -polymer composite cylinders was demonstrated.

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