

Nanocomposites from Coated Nanoparticles

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1. Introduction

Nanomaterials consist of particles with diameter less than 100 nm, and they exhibit special physical or mechanical properties related to this small dimension. A nanocomposite is a material composed of two or more phases, one of which has a grain size of less than 100 nm. Here the combination of different physical or chemical properties may lead to completely novel materials. The grain size limit of 100 nm is general, but most phenomena related to grain size are restricted to particles with sizes below 10 nm. Since the pioneering work of Gleiter^[1-3] many research groups have contributed to synthesis^[4-9] and properties^[10-15] of nanomaterials and nanocomposites. Several methods of synthesis, such as inert gas condensation,^[4,5] the sol gel process, or microwave plasma processing,^[6-9] were developed to produce nanomaterials.

Except for properties related to grain boundaries^[10,11] most of the physical properties of interest are those of non interacting isolated particles.^[12-15] Such properties can be measured in extremely dilute suspensions. For technical applications, one needs a dense body composed of nanoparticles that can be handled while still exhibiting the special "nano" properties. Even when the sintering activity of compacted nanoparticles is high, standard procedures of powder metallurgy, such as pressing and sintering, are almost impossible to perform if the material is to retain its nano properties. The main reason for this is that grain growth occurs during sintering or heat treatment, increasing the particle size (up to a few hundred nanometers). Thus the properties related to the small grain size are lost. Moreover, many of these special properties stem from isolated particles. In a sintered body, even at the right grain size, the particles interact. In many cases this destroys the intended special properties.

Nanocomposites can solve these problems. In an ideal nanocomposite, which is similar to a suspension, the active nanoparticles (i.e., the carriers of the desired property) are well separated. Theoretically, such composites could be produced by the mechanical blending of two or more powders. However, due to the aggregation of nanoparticles by

van der Waals forces, such processes never lead to isolated particles. The application of wet chemical methods is better, but not always successful. The best way to solve the problem is to coat the nanoparticles. The coating has to be applied before the particles get a chance to agglomerate by van der Waals forces. The microwave plasma synthesis process is well suited to solve this problem.

2. Synthesis of Coated Nanoparticles

Gas phase reactions can be used to synthesize nanoparticles. Classically these processes have been limited to small production rates in order to avoid agglomeration. Agglomeration is due to a high concentration of particles in the aerosol. Additionally, these agglomerates will sinter immediately to hard ones, because of the high temperatures (800 to 1200 °C) needed to overcome the activation threshold in the system. Such processes are not well suited to produce large amounts of coated nanoparticles, if the individual particles, not the clusters are to be coated. A gas phase process capable of coating the individual particles at sufficiently high production rate is the microwave plasma process.

The basic idea of this new process is a gas phase reaction performed in a plasma powered by microwaves. The plasma is generated in a reaction glass tube made of quartz, passing a resonant microwave cavity.^[7] Precursors like chlorides, carbonyls, or organometallic compounds are evaporated outside the reaction tube and inserted as vapor into the system. Depending on the product in question, reaction gas mixtures of Ar/20 vol. % O₂, N₂/4 vol. % H₂, or Ar/1 vol. % H₂S are used. In the plasma the reactants are partly ionized or dissociated. This is a highly activated state. Therefore, thermodynamically possible but kinetically thwarted reactions can be performed at relatively low temperatures.

Since energy transfer E to a charged particle in an electrical oscillating field is inversely proportional to its mass m and the square of the microwave frequency f^2 , significantly more energy is transferred to electrons than to ions or radicals. This leads to relatively low overall temperatures in the system, compared to conventional gas phase reactors. Two standard industrial frequencies are available: 2.45 GHz and 0.915 GHz. The temperature (measured directly behind the plasma zone) can be adjusted to between 100 and 500 °C (for 2.45 GHz equipment) and to between 300 and 800 °C

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using the 0.915 GHz equipment. The pressure can be selected from 10 to 50 mbar. Pressure and gas flow are chosen so that the residence time of the particles in the plasma zone is a few milliseconds. This short residence time in the reaction zone keeps the size distribution of the particles very narrow. With increasing pressure, the energy transfer to the plasma increases to the point where the thermal collision frequency in the gas is equal to the microwave frequency.

Besides the low reaction temperature, there is a further feature characteristic to the microwave plasma process: After leaving the plasma zone the particles carry electrical charges with the same sign, which prevents the formation of agglomerates. Therefore the particles are transported individually in the gas. This makes it possible to coat the particles in a second reaction step. Together, electrical charging of the particles and the low temperature prevent the formation of hard agglomerates. After cooling and decharging of the particles the formation of soft, van der Waals bond agglomerates is still possible.

Coating of the particles is performed in a second reaction zone.^[8] In this plasma zone, the particles formed in the first reaction step act as nuclei for the condensation of the coating phase. As the gas kinetic cross section of a particle is about three orders of magnitude larger than that of a single molecule, the probability of forming new particles by homogenous nucleation from precursor 2 is extremely small. Figure 1 depicts the synthetic procedure for ceramic coated nanoparticles. Two microwave reactors are connected consecutively on one reaction tube. The precursors are introduced immediately in front of the reaction zones where the chemical reactions take place. The powders are collected on cooled walls by thermophoresis.

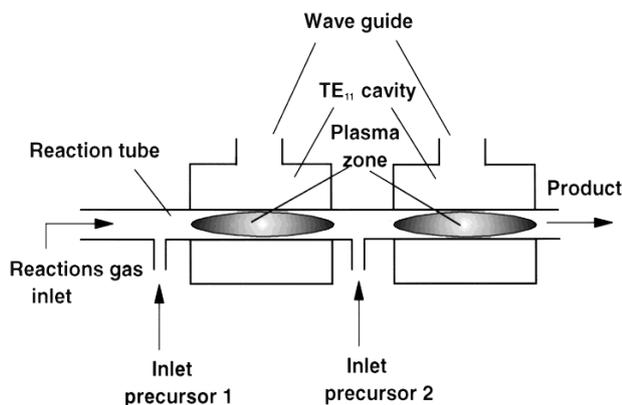


Fig. 1. The process used to synthesize ceramic-coated ceramic nanoparticles.

For polymer coating in general the same set up is used.^[9] In this case, the monomer is introduced as a vapor directly after the last plasma zone where the nanoparticles are formed or coated. The monomer condenses on the surface of the ceramic particles and polymerizes under the influence of the heat and UV radiation emitted by the plasma. To perform this process proper temperature adjustment is crucial.

3. Morphology and Properties of Coated Nanoparticles and Nanocomposites

3.1. Morphology

Figures 2 and 3 show electron micrographs of coated nanoparticles. The particles in Figure 2 are coated ceramically, whereas polymer coated ones are depicted in Figure 3. In both cases the features kernel and coating are easily visible, because the coating is made of material with lower atomic number than the core. Figure 2 shows particles where a crystallized core, characterized by lattice fringes, is surrounded by an amorphous layer. Generally the same is visible in Figure 3. Also in this case the coating is visible as a halo around the kernel. The polymer used in this case is poly methacrylic acid (PMA). The ceramic content in this case is approximately 20 vol. %. In both figures one observes a very regular coating of the surface with the second phase.

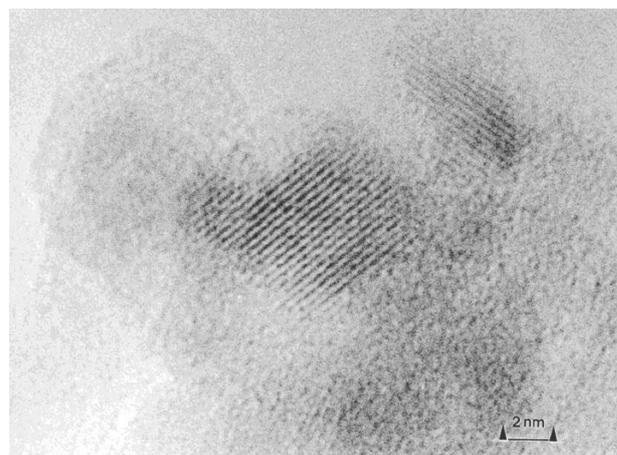


Fig. 2. Zirconia, ZrO_2 -alumina, Al_2O_3 nanocomposite. The crystallized zirconia core, characterized by lattice fringes, is coated by amorphous alumina. The thickness of the alumina coating is ca. 1 nm.

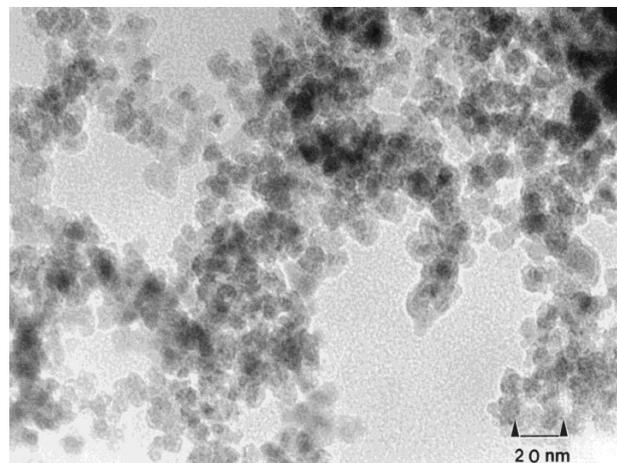


Fig. 3. Morphology of polymer-coated γ - Fe_2O_3 (maghemite) nanoparticles. The dark parts are the maghemite kernels, while the coating is represented by the halo around the kernels. Note the uniform size of the cores.

Compaction of such a powder is easy. Provided that core and coating show no mutual solubility, ceramic coated pow

der can be pressed and sintered at high temperature to obtain technical parts. This is simpler in the case of polymer coated particles, as pressing with about 0.7 Pa at a temperature in the range from 100 to 120 °C results in parts with sufficient strength. The structure of such a densified ceramic polymer composite is shown in Figure 4. In this case, the ceramic kernels consist of γ Fe₂O₃ (maghemite), the coating of PMA. This sample contains 50 vol. % ceramic. Therefore the polymer coating is very thin (approximately 1 nm) and is not visible in this electron micrograph. The main feature visible in this micrograph is the very narrow size distribution of the maghemite particles and their regular arrangement. This is of great importance, as the superparamagnetic properties are volume dependent. A comparable structure is found in nanocomposites made of ceramic coated ceramic particles.

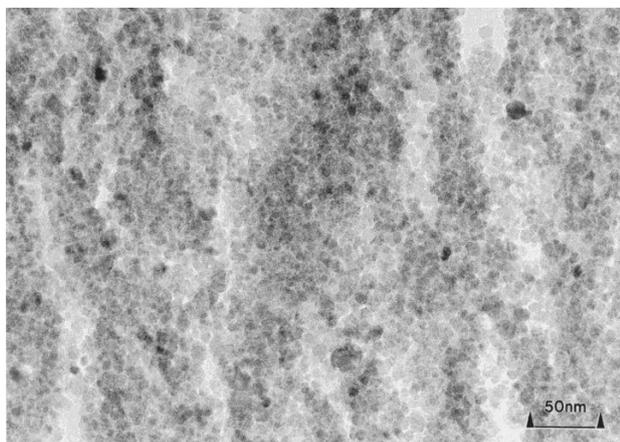


Fig. 4. Structure of a hot pressed maghemite-polymer composite. The texturing is an artefact from cutting the specimen in an ultramicrotome. The thickness of the specimen is 20 nm.

3.2. Properties

As an example of a property unique to nanocomposites, superparamagnetism was selected. Superparamagnetism exploits the phenomenon of the thermal instability of a property resulting from small particle size. The basic principle of this phenomenon is the following: Let us assume a property P of a material that depends on the size s (surface, volume, etc.) of the specimen. To change this property, energy input proportional to property dependent constant $K(P)$ and the particle size is necessary. If this energy $K(P)s$ gets smaller than the thermal energy of the particle kT (k Boltzmann constant, T temperature), then thermal energy is sufficient to change the property. There is no additional energy input necessary. Therefore, the property P fluctuates thermally.

Looking at magnetic properties of small single domain particles, the property in question is the orientation of the magnetization vector, within the particle at zero field. To rotate the vector of magnetization the energy KV ($K =$ con-

stant of anisotropy, $V =$ particle volume) is necessary. The condition $KV < kT$ describes the onset of superparamagnetism. At temperatures $T > KV/k$ the material is superparamagnetic. In this state the vector of magnetization fluctuates thermally. Therefore, superparamagnetic material is free of hysteresis. The description given above is valid for one particle only. It must not be applied to an ensemble of particles. If two or more superparamagnetic particles are touching each other these particles will act like a large one. Superparamagnetism is lost. To avoid magnetic interaction, it is necessary to keep the magnetic particles at a distance. Therefore, superparamagnetic technical parts can be realized only with nanocomposites composed of coated nanoparticles, where the coating consists of non magnetic material.

It may be interesting to note that besides zero coercivity superparamagnetism has a more important advantage. In conventional soft magnetic materials, the maximum frequency of application is limited by the resonance of the Bloch walls. As superparamagnetic materials are free of Bloch walls, the limiting frequency is determined by electron spin resonance. This frequency is at least one order of magnitude higher.

Figure 5 shows the magnetization curve of two superparamagnetic ferrite pellets. For both ferrites, γ Fe₂O₃ and

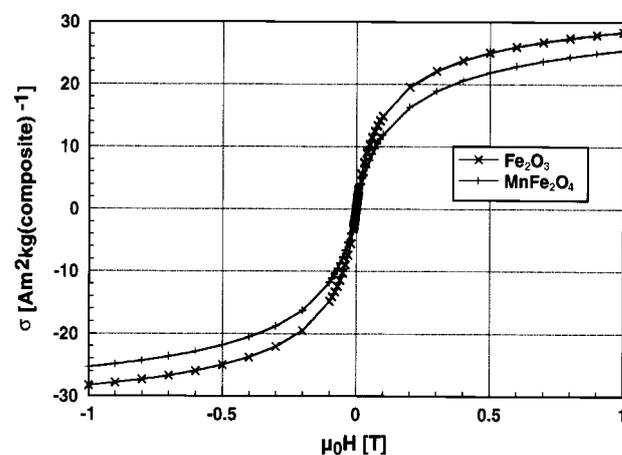


Fig. 5. Magnetization curves determined on γ -Fe₂O₃-PMA and MnFe₂O₄-PMA pellets at 300 K. The magnetization curves are characterized by a zero remanence.

MnFe₂O₄, the zero coercivity is obvious. The magnetization curve is free of any hysteresis. This is not only true for quasi static measurements, but also for dynamic ones. The classic dynamic proof for superparamagnetism is the Mössbauer effect. Normal magnetic materials show a sextet of lines, whereas non magnetic and superparamagnetic materials are characterized by the quadrupole split doublet. The magnetic sextet is not found in superparamagnetic materials, because the fluctuation frequency of the magnetization vector is larger than the Lamor frequency of the nucleus, which is in the range of 10⁷ to 10⁸ Hz. A typical example of a Mössbauer spectrum of a superparamagnetic material is

given in Figure 6.^[16] This high frequency behavior is not only found in the Mössbauer effect, but also in the susceptibility, a property crucial for technical application. Figure 7 depicts preliminary results of the dependency of the real

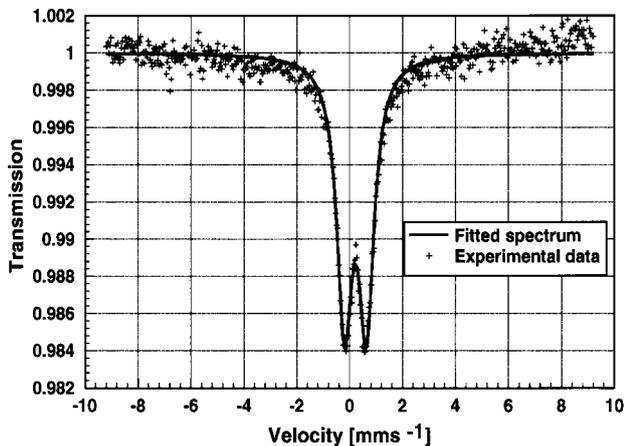


Fig. 6. Mössbauer spectrum of a superparamagnetic $\gamma\text{-Fe}_2\text{O}_3\text{-PMA}$ composite. The quadrupole split doublet is typical for superparamagnetic materials.

(m') and imaginary (m'') part of the susceptibility in the frequency range from 20 kHz to 2 GHz for a hot pressed $\text{MnFe}_2\text{O}_4\text{-SiO}_2$ composite. Besides some scatter of the data, it is obvious that at least in this frequency range a res

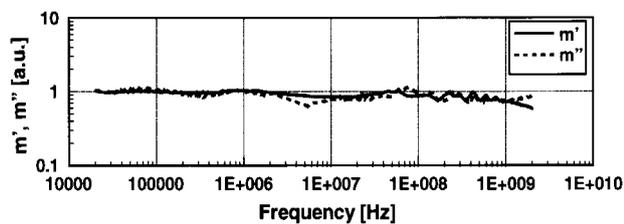


Fig. 7. Real (m') and imaginary (m'') part of the susceptibility of a hot pressed $\text{MnFe}_2\text{O}_4\text{-SiO}_2$ ring with 3.5 mm diameter. It is obvious that there are no resonances in the frequency range up to 2 GHz.

onance limiting the frequency of application is not found. The material tested was a ring of a composite part with an outer diameter of 3.5 mm. An application of this new ferrite material is found in cellular phone systems replacing the expensive and lossy surface wave resonance filters.

4. Summary

A new type of starting material for nanocomposites, coated nanoparticles is now available. This material is synthesized using the microwave plasma process. In a nanocomposite made from this powder, it can be guaranteed that the kernels are isolated. This enables the production of technical parts with properties characteristic for isolated particles. This opens a route for new high value added products. Superparamagnetism was described as an example application for these advanced materials.

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