Coated nanoparticles: A new way to improved nanocomposites

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Abstract

This paper introduces the new concept of coated nanoparticles as starting material for improved nanocomposites. The very special properties of nanomaterials often are properties of isolated particles. After combining nanoparticles to a macroscopic workpiece, usually these special properties are lost. Therefore, to obtain macroscopic parts exhibiting the properties of the isolated particles it is necessary to avoid or at least reduce the interaction of the particles. This can be achieved by coating each individual particle with a second ceramic or polymer layer. This type of materials can be synthesised only by using the microwave plasma process, because in this process the particles leave the plasma zone with electrical charges thwarting agglomeration. Additionally, by proper selection of the coating material it is possible to avoid grain growth during densification of the powder by sintering or hot pressing. As an example of application and as a proof of concept, the properties of macroscopic superparamagnetic parts are explained. Possibly, coated nanoparticles are the only starting material to produce macroscopic parts showing the very special properties of nanomaterials.

Introduction

Nanomaterials are materials with particle respectively grain sizes below 100 nm and special properties directly connected to the small grain size (Gleiter, 1989, 1992). Compared to materials with grain sizes in the micrometer range nanomaterials excel in different or even new properties. Nanocomposites – as they are described in this paper – are composite materials with at least one phase exhibiting the properties of a nanomaterial. Additionally, it is assumed that there is a random arrangement of the nanoparticles in the composite.

Often the special properties of nanomaterials are properties of single, isolated particles. Therefore, combining a large number of nanoparticles to a macroscopic part may destroy the properties that are characteristic for these particles. Preparing a macroscopic part from a powder is done by pressing and sintering. During sintering, a high temperature treatment, grain growth is unavoidable. This may destroy the special properties. Coating each individual particle with a thin layer of a second phase solves these problems. The range of applications for nanomaterials will even be broadened as this coating changes the surface chemistry of the particles. Additionally, as kernel and coating material are homogeneously distributed on a nanometer scale some properties of a densified solid can be changed gradually with the thickness of the coating. Depending on the requirements of the system in question, the coating material may be ceramic or polymer. By coating nanoparticles with a second layer, the following improvements are obtained:

- The kernels are kept on a well-defined distance. Therefore, the interaction of the particles can be adjusted.
- During sintering, the growth of the kernels is thwarted.

- The surface chemistry of the particles can be adjusted according the needs for application.
- The mixing of the two phases is homogenous on a nanometer scale.

Coated nanoparticles can be produced using the microwave plasma process. This is possible, because the particles leave the plasma zone with high electrical charges of the same sign avoiding agglomeration. Other gas-phase processes like the inert gas condensation (Hahn, 1988) or the conventional chemical vapour synthesis process (Chang, 1994) are not capable to produce non-agglomerated coated nanoparticles.

Synthesis and morphology of coated nanoparticles

The principles of the microwave plasma synthesis

Microwave plasma synthesis of nanoparticles is based on gas phase reactions in a non-equilibrium plasma (Vollath, 1992). A microwave plasma is not in equilibrium because the energy E transferred to a charged particle with the mass m in an oscillating electrical field with the frequency f is:

$$E \propto \frac{1}{mf^2} \tag{1}$$

From formula (1), it is evident that there is more energy transferred to electrons with their small mass as compared to ions or radicals. Additionally, in a plasma environment the collision frequency z with the uncharged molecules and atoms in the gas phase has to be taken into account.

$$E \propto \frac{1}{m} \frac{z}{f^2 + z^2} \tag{2}$$

As the collision frequency z increases with increasing gas pressure, the energy transfer as a function of the gas pressure exhibits a maximum at $f = z$. Stable operating conditions can be found in the pressure range below this maximum.

For experimental realisation the standard industry frequencies 0.915 and 2.45 GHz are selected. From the formulae (1) and (2) one realises that 2.45 GHz is in those cases of advantage, where the temperatures have to be kept as low as possible. On the other hand, the main advantage of 0.915 GHz can be seen in the larger dimensions of the wave-guides, allowing the application of large sized reaction tubes.

In the technical realisation of the microwave plasma process, a long reaction tube made of quartz glass passes a resonant TE_{01} or TE_{11} cavity. At the intersection of the reaction tube and the resonator, a microwave plasma is ignited. The precursors, chlorides, carbonyls or metal organic compounds, are introduced as vapours into the reaction tube directly in front of the plasma zone. In the plasma zone the precursor will be partly dissociated and ionised. This reduces the activation energy to initiate the reaction with the reaction gas and makes the reaction possible at a low temperature. The temperature in the plasma zone, the reaction temperature, can be adjusted in the range from 100°C to about 800°C. The pressure in the system is adjusted from 30–80 mbar in the case of the 0.915 GHz and from 5–20 mbar in the case of the 2.45 GHz plasma. The residence time in the reaction zone controlling the particle size of the product is in the range from 5 to 15 ms, depending on the pressure in the system. After leaving the reaction zone, the particles are carrying electrical charges with the same sign. This, in combination with the low reaction temperature, reduces the probability for the formation of hard agglomerates. The formation of van der Waals bond agglomerates unavoidably occurs during collection on cold surfaces. Table 1 gives an overview of the reaction gases necessary for different products.

As an example for such a reaction product, Figure 1 shows ZrN particles (Vollath, 1993) with a very narrow particle size distribution around 5 nm.

Ceramic coated nanoparticles

Taking advantage of the electrical charge of the as-produced nanoparticles it is possible to coat the individual particles with a second layer as long as they are not precipitated from the gas stream. Figure 2 exhibits a schematic drawing of a system for the synthesis of coated nanoparticles (Vollath, 1994a,b). The system for synthesis consists of a long reaction tube passing two microwave cavities. At the intersection between

Table 1. Reaction gases

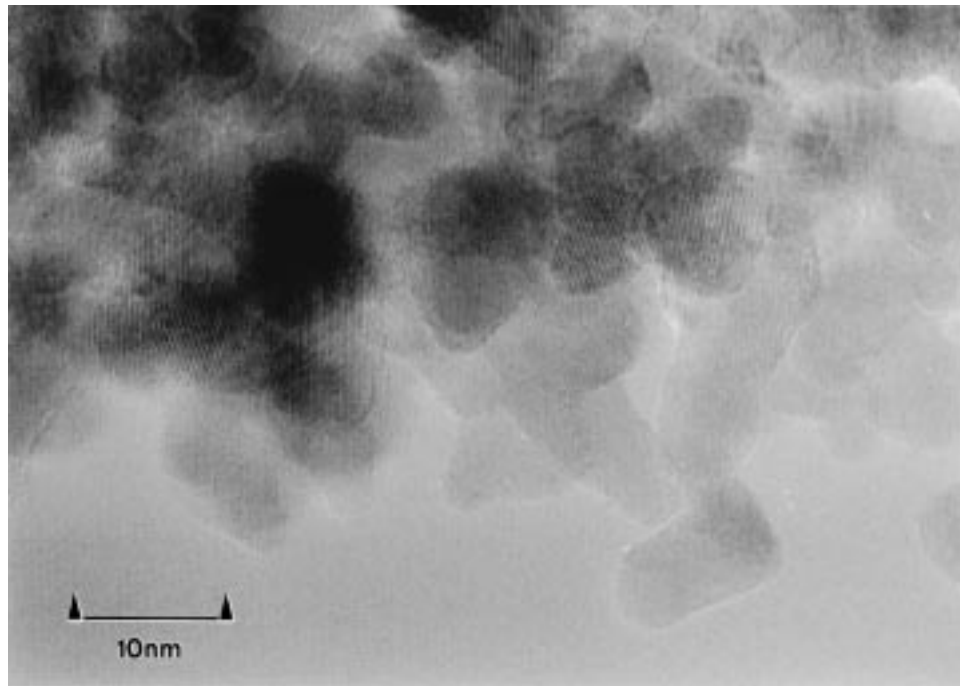| Product	Reaction gas
Oxides	Ar, 20 vol% O_2
Nitrides	N_2, 4 vol% H_2
	N_2, 1 vol% NH_3
Sulphides	Ar, 1 vol% H_2S
Metals	Ar, 4 vol% H_2

Figure 1. Nanocrystalline ZrN particles. The particle were produced in a 0.915 GHz microwave plasma at 750°C and a pressure of 50 mbar.
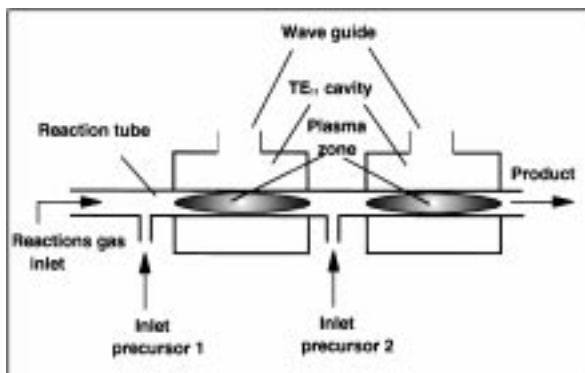

Figure 2. Schematic drawing for the arrangement to synthesise ceramically coated ceramic nanoparticles.

the microwave cavities and the reaction tube is the plasma zone. Both precursors are introduced into the reaction tube directly in front of the plasma zones. In this case the particles formed in the first step act as seeds for the condensation of the second phase. As the gas kinetic collision cross section of such a nanoparticle is up to three orders of magnitude larger than the one of a molecule or ion, the probability of coating is also larger than the probability of the formation of a

new nucleus. Therefore, all particles formed in step 1 will be coated in the second reaction zone; the probability of the formation of pure particles in the second step is very small. The thickness of the coating can be adjusted by the process parameters.

To obtain good coatings the following conditions have to be fulfilled:

- Both components must not have a mutual solubility.
- The components should not form a common compound.
- The surface energies of the two components must be in a range that the second component is able to coat the kernels formed in the first step. Usually, this condition is fulfilled in ceramic/ceramic or ceramic/polymer systems. In the case of metal/ceramic systems, it may happen that the metal is not wetting the kernel. In this case, one obtains a decoration of the surface with metal clusters instead of a coating.

Figure 3 depicts a micrograph of a coated particle. In this case the core consists of about 3–5 nm zirconia, ZrO_2 particles. The coating consists of amorphous alumina, Al_2O_3. By EDX in a dedicated STEM the existence of the coating was proven (Szabó, 1994).
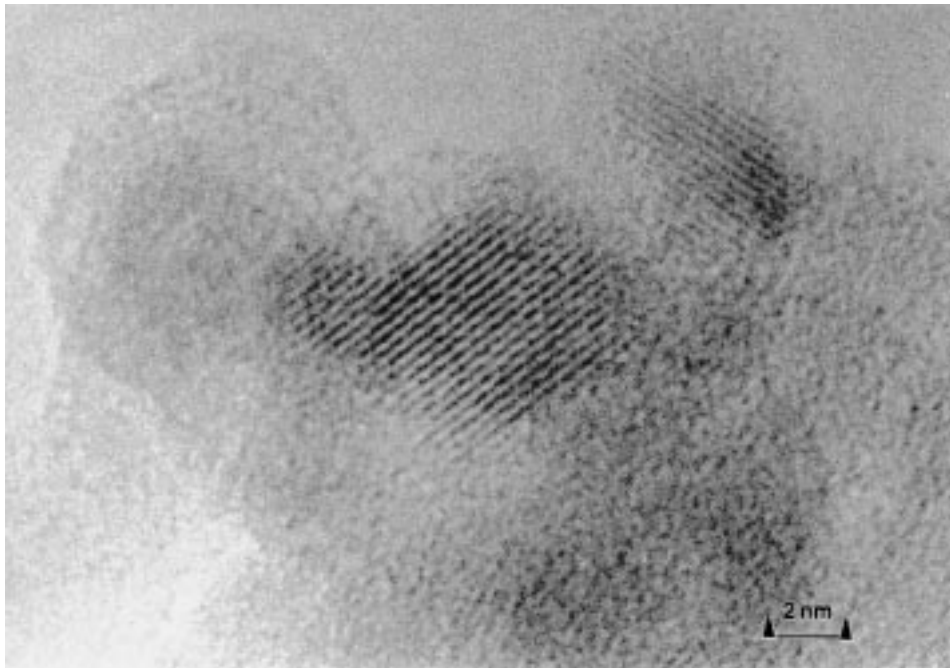
Figure 3. Crystallised ZrO_2 particles coated with amorphous Al_2O_3, produced at 500°C and 80 mbar with 0.915 GHz.

The appearance of these coated particles is different if kernel and coating are crystallised (Vollath, 1994b). An example for such a particle is depicted in Figure 4. In this figure a maghemite, γ-Fe_2O_3 particle coated with zirconia is shown. Because of the better contrast, one sees primarily the lattice fringes of the coating. In the centre of the particle, the lattice fringes are no longer visible. This is because the maghemite crystallises in a different structure with different lattice fringes.

Polymer coated nanoparticles

In many applications of nanoparticles, parts made out of them are loaded neither thermally nor mechanically. Therefore, it is not necessary that such a part consists of a high strength ceramic. Rather, polymer bond parts are sufficient. Similar like coating with a ceramic material, coating with a polymer is done directly after the synthesis in a plasma zone before the particles are collected (Vollath, 1997a).

Figure 5 shows a sketch of the arrangement to produce nanoparticles coated with a polymer. In a first step, the ceramic particles are synthesised in a microwave plasma zone. The operating conditions are selected to keep the temperatures as low as possible. After the

plasma reaction zone, the monomer is introduced. The criteria for the selection of the monomers are:

- It must be stable at the temperatures after the reaction zone.
- It must polymerise immediately under the influence of temperature and the UV radiation stemming from the plasma.

Provided the temperature is adjusted properly, the monomer condenses at the surface of the particles and polymerises under the influence of the UV radiation. The monomers with the best performance in this respect are methacrylic acid (MA) and methyl methacrylate (MMA). Figure 6 shows γ-Fe_2O_3 particles coated with PMMA. Similar as in the case of ceramically coated particles one realises a uniform distribution of polymer at the surface. In the special example depicted in Figure 6 the polymer coating is extremely thick. Otherwise it would be nearly impossible to show the polymer coating in a micrograph. Gel permeation chromatography (GPC) is used to determine the degree of polymerisation (Vollath, 1999). The GPC plot of an Al_2O_3/PMMA specimen depicted in Figure 7 shows maxima around 500 and 1000 da, which are equivalent to about 5 respectively 10 masses of the monomer. This is an extremely low degree of
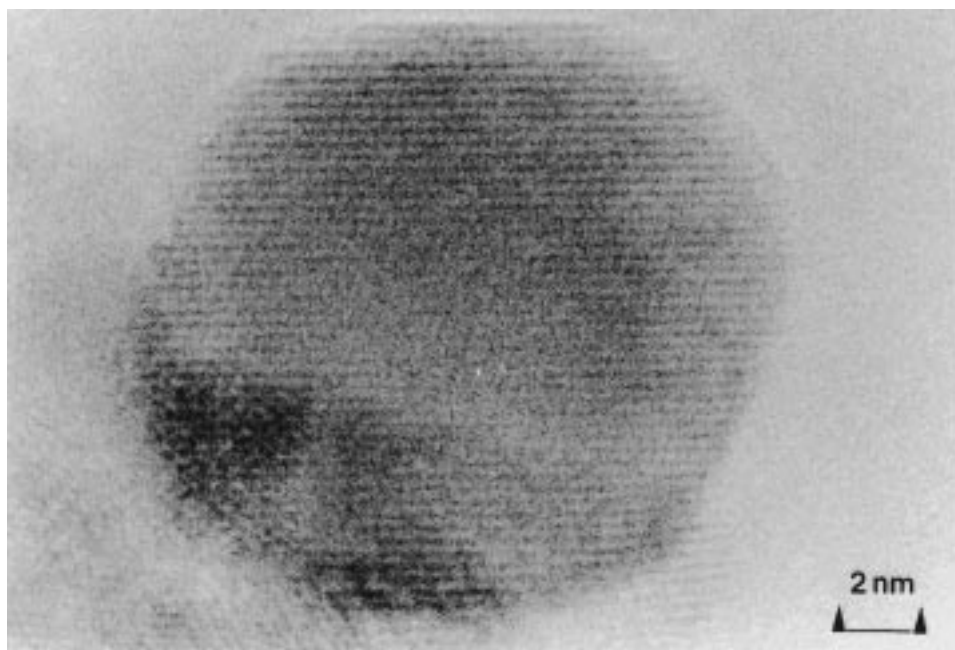
Figure 4. Crystallised Fe_2O_3 particles coated with crystallised ZrO_2. The particles were synthesised at 570°C and 40 mbar in a 0.915 GHz equipment.
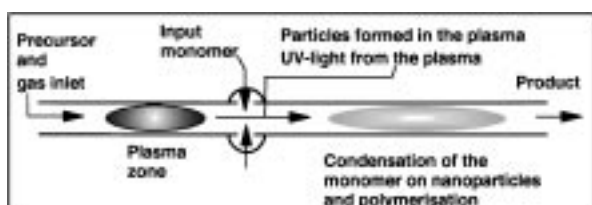

Figure 5. Schematic drawing of the arrangement for polymer coating of ceramic nanoparticles.

polymerisation. Evaluating these numbers, one has to take into account that the polymerisation is limited by geometrical factors in a layer with a thickness of 1 or 2 nm on a 5 nm particle. Additionally, the chemistry in the gas phase after the plasma zone may not be favourable for the formation of long chains.

Morphology and properties of solids made of coated nanoparticles

Morphology

Solids of ceramically coated nanoparticles are prepared by cold pressing and subsequent high temperature microwave sintering at 1200°C for 15 min, whereas polymer coated particles are consolidated by pressing in the temperature range from 70°C to 140°C.

Figures 8 and 9 show typical morphologies of the consolidated materials of both kinds. The ZrO_2 particles in Al_2O_3 matrix (Figure 8) exhibit astonishingly small particle size of less than 10 nm. The starting material for this specimen consisted of 5–8 nm ZrO_2 particles coated with 2–3 nm Al_2O_3. The initially amorphous Al_2O_3 coating forms the matrix of the composite. It crystallised into the α-phase with particle sizes in the micrometer-range during sintering. At this place it is important to point out that even if the alumina shows dramatic grain growth, nearly no grain growth is observed in the ZrO_2 particles. This is, because the mutual solubility of the oxides in question is very small. The specimen for electron microscopy was prepared by dimpling and ion milling of diamond cut and polished disks (Schloßmacher, 1996). The appearance changes dramatically in the case of the composite shown in Figure 9. This material, a γ-Fe_2O_3/PMMA composite with 50 vol% polymer was consolidated at 100°C under a pressure of 1.4 MPa. Because of the low temperature during consolidation, any grain growth or reaction between the two phases of the composite is suppressed. The layered structure of the material, visible in this micrograph, is an artefact of the specimen preparation.
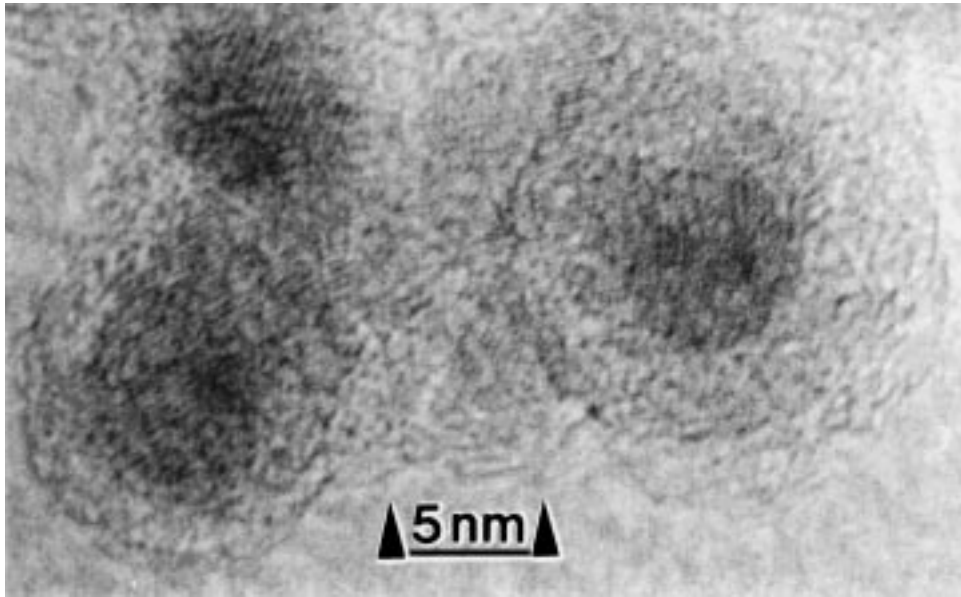
Figure 6. PMMA coated Fe_2O_3 particles, produced at 130°C and 8 mbar in a 2.45 GHz microwave plasma. The ceramic content of this material is 20 vol%.

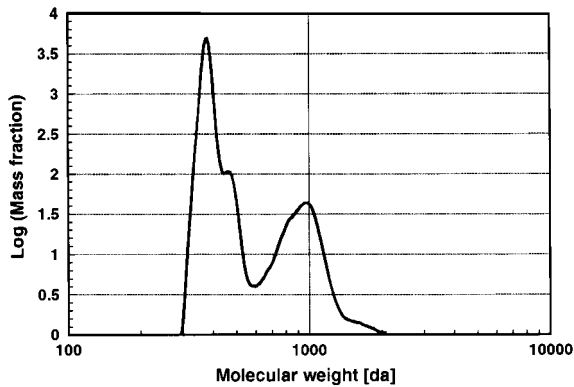*Figure 7.* Distribution of molecular masses in the PMMA coating of Al_2O_3 nanoparticles.

In this case, the specimen for electron microscopy was prepared by cutting with an ultramicrotome. The thickness of the specimen was 20 nm. It is obvious from Figure 9 that the distribution of particle sizes is in a very narrow range.

Properties

As example of a property that can be obtained only with nanocomposites, the magnetic properties of ferrites are selected. Non-interacting nanoparticles of ferrites may be superparamagnetic. Superparamagnetic materials excel in zero magnetisation losses. Provided the sizes of the particles are sufficiently small and fulfil the condition

$$Kv < kT \qquad (3)$$

(K – constant of magnetic anisotropy; v – volume of the particle; Kv – energy of magnetic anisotropy; kT – thermal energy) the material is superparamagnetic (Neél, 1949; Vollath, 1997b). An essential condition for superparamagnetism is that the particles are not interacting. Interaction via the dipole moments of the particles leads to magnetically large particles that are not longer superparamagnetic. This phenomenon is demonstrated in Figure 10 comparing the magnetisation curves of γ-Fe_2O_3 and γ-Fe_2O_3 coated with a 1 nm ZrO_2 layer. It is obvious that the magnetisation curve of the bare material shows some hysteresis, whereas the coated material is free of any hysteresis. The materials in Figure 10 show extreme small particle sizes; therefore, the magnetisation is extremely low. After slight increase of the particle size, the magnetisation increases. This has been shown in polymer coated ferrites (Vollath, 1999). The property essential for technical application in the communication industry is the susceptibility. Figure 11 depicts the frequency dependence of the susceptibility of different ferrite based spinelle/PMMA composite in comparison to a commercial ferrite. The essential information from this
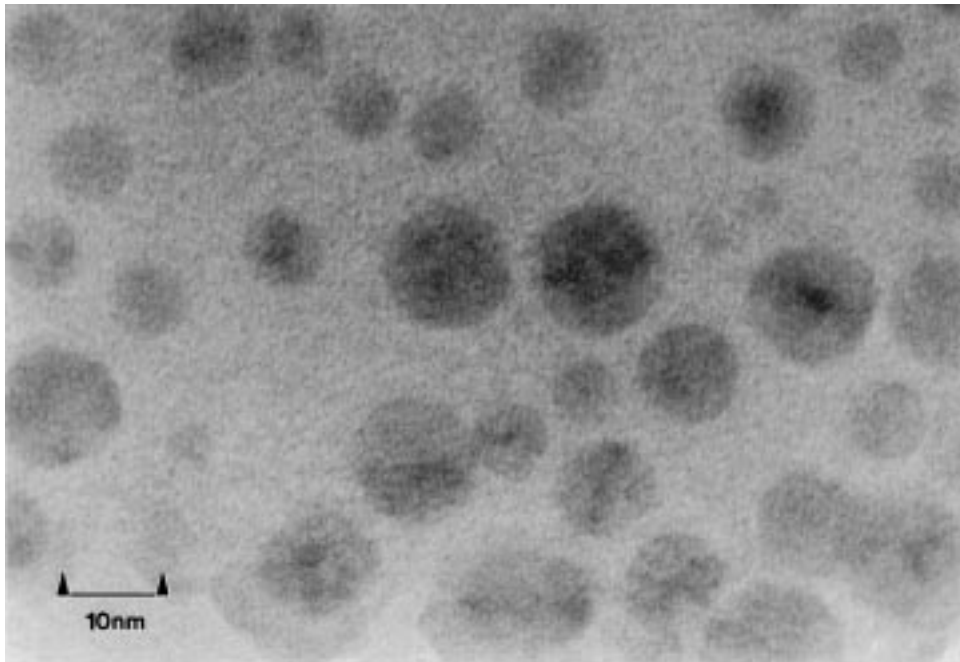
Figure 8. Morphology of sintered material made of Al_2O_3 coated ZrO_2 particles. The starting powder was produced in a 0.915 GHz equipment at 520°C and 30 mbar. The sintering of the densified body was performed by microwave sintering at 1200°C for 15 min.
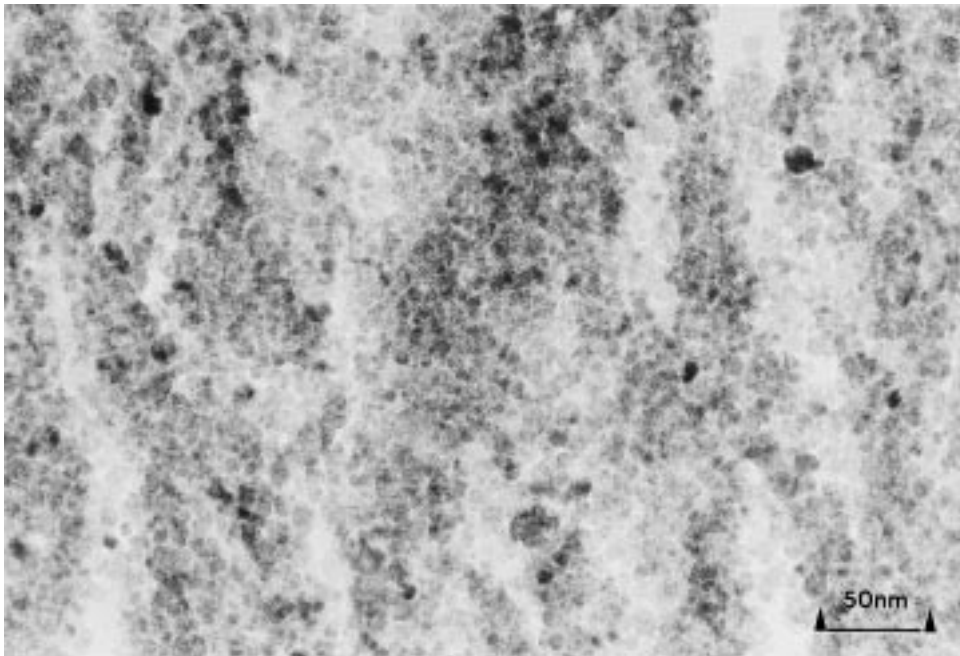
Figure 9. Hot pressed ceramic/polymer composite made of PMMA coated Fe_2O_3 particles. The ceramic content of this material is 50 vol%. The layered structure is an artefact from cutting the sintered material with an ultramicrotome.
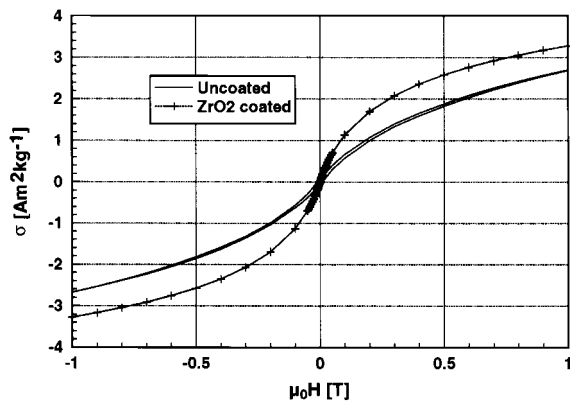
Figure 10. Comparison of the magnetisation curves of nanocrystalline γ-Fe$_2$O$_3$ uncoated and coated with ZrO$_2$.
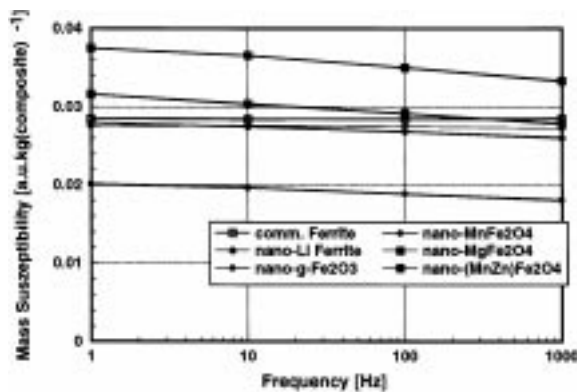

Figure 11. Mass susceptibility of different ferrite/polymer compositions in comparison to a commercial ferrite.

figure is that for application the superparamagnetic material is comparable to today's commercial ferrite. Additionally, superparamagnetic ferrites have advantages over 'classical' ferrites due to lower losses and higher maximum frequencies for application.

Conclusions

This paper introduces the concept of coated ceramic nanoparticles as starting materials for improved nanocomposites. Synthesis of this special type of material is possible only with the microwave plasma process. It was demonstrated that this coating might be a ceramic or a polymer one. Nanocomposites made of coated nanosized kernels have the advantage over nanocomposites made from mechanically blended powder that there are no kernels in direct contact. Therefore, it is possible to produce macroscopic parts exhibiting properties characteristic for individual nanoparticles. The material for the coating may be – depending on the application – a ceramic or a polymer one. The special properties of these materials were demonstrated in the systems Fe$_2$O$_3$/ZrO$_2$ and Fe$_2$O$_3$/PMMA. In these cases, macroscopic bodies with superparamagnetic properties were obtained. These properties are not possible with conventionally produced composites.

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