Nano technology is one of the keywords of modern ceramics. It is a curious fact that ceramists have worked in fact with nano particles since time out of mind: clays contain extremely fine colloidal particles giving e.g. the plasticity, which is necessary for plastic moulding. Even certain ceramic or glass colours of the middleage have used nano particles – without knowing details of their size and action. The "new wave" of the last decades has made nano particles, a world between atoms and the macroworld, interesting for chemists, biologists, material specialists and others. The articles in technical publications and the presentations in conferences have brought some knowledge about this microworld to ceramists, but it often just scratches the surface. The following paper is written by a team of R&D-specialists, working in the Southwest of Germany at the Institute for New Materials (INM) headed by Prof. Dr. rer. nat. Helmut Schmidt, a worldwide esteemed pioneer in this special area.

Sm 2004/1

Potential of Ceramic Nanoparticles

H. Schmidt, K.P. Schmitt, F. Tabellion, R. Drumm*

1 Introduction

For processing of ceramic powders, the particle size, particle shape and particle distribution has high importance, since many processing parameters and final properties are influenced. Particle size distribution influences the green density, the pore size distribution of the green body, the sinter activity as well as grain growth, at last the grain size distribution in the sintered material.

It is a well known fact, that surface atoms, surface ions or surface molecules show a free energy value different from that of the inside of a particle. This is due to the change of local environment while approaching the surface. The bonds become weaker and the lattice parameters change, which can be easily detected by X-ray diffraction patterns, leading to an increase of the half width of the X-ray peaks. This is used to calculate primary particle size by the Sherrer's equation.

The different state of atoms close to the surface for example leads to the enhanced diffusion compared to the lattice diffusion. For this reason surface diffusion is one of the most important densification mechanism during the sintering process. This indicates that the overall properties of particles change remarkable with decreasing diameter.

Diameter and surface area depend on a square root function, the volume varies by the third order of magnitude. Since the "disordered shell" around a small particle is not a monolayer but comprises a certain volume, the volume fraction of this "shell" also increases by the third order

of magnitude with decreasing diameter. This has to be taken into consideration if one looks at the change of properties with a decreasing particle size.

Reducing the diameter from 10 µm to 10 nm, the surface area increases by 6 orders of magnitude, if the overall material volume is kept constant, and the disordered shell volume increases by 9 orders of magnitude. This phenomenon has been described in detail in the book of Gleiter [1].

Many properties are affected by decreasing the particle size. Beside the disordered shell volume, for example, in semiconductors quantum confinement takes place leading from band gap structures to exitons, which has been investigated in detail by Henglein [2] and Weller [3]. In metal particles, plasmon resonances are observed, based on the resonance of hot surface electrons. This leads to an intensively coloured transparent system if the particles are homogeneously distributed in a transparent matrix, and this is known since centuries for example from gold ruby glasses.

Gold also shows a strong non linear optical behaviour [4] of the third order which was investigated for optical switching. Magnetic properties also can change with size, for example the change from ferromagnetism to super-paramagnetism which for example is well known in nano magnetite and nano maghemite.

Not only the disordered shell volume is increased significantly with reduced particle size, but also the interface either to a liquid or a solid as surrounding medium in which the particles are dispersed. This interface, in general, has a different molecular structure than a con-

* Prof. H. Schmidt, Dipl.-Ing. K.P. Schmitt, Dr. F. Tabellion, Dipl.-Ing. R. Drumm – Institut für Neue Materialien gem. GmbH, Im Stadtwald, Gebäude 43, D-66123 Saarbrücken – www.inm-gmbh.de
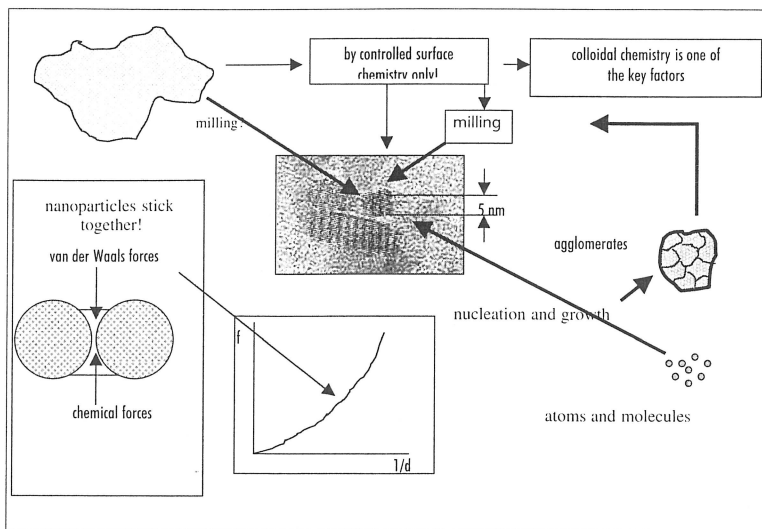
Fig. 1
The different approaches to nanoparticles bottom up versus top down

tinuous bulk phase of the matrix and in analogy to the disordered shell of the particle the interfacial phase volume also is increasing with decreasing particle diameter.

For ceramic materials one of the most interesting aspects resulting from a very small particle size, is the potential of reducing the sintering temperature. The dependence of the sintering temperature on particle size is well investigated, but investigations about particle sizes in the lower nanorange are very difficult to perform due to serious processing drawbacks.

20 years ago, many investigations have been carried out to prepare ceramic components by sol-gel techniques. It is a matter of fact, that the sol-gel technique in a general view represents a nanoparticle technology, because e. g. for ceramic systems sols represent nanoparticles dispersed in a liquid phase. To stabilize those sols, forces between the particles (van der Waal forces, hydrogen bonds) have to be overcome by keeping the particle in a distance greater than the critical distance. This, in general, is achieved through electrostatic forces by charging the particle surfaces.

This phenomenon is well known and has been described by Stern [5] already at the beginning of the 20th century and is used as the basis of the DLVO-theory . For having a measure for the particle surface charges, the so called ζ-potential is determined. The critical distance is the distance at which the repulsion force (due to the charge) changes into an attraction.

The formation of a green body from sols in general is obtained either by removal of the particle charge at the point of zero-charge through a appropriate pH-change or by evaporating the solvent. In general, this leads to a green body in form of a gel with a very low green density, ranging from a few to about 20 %. Processing these "nanoparticulate" gels to large bodies leads to serious problems, so that this technology mainly has been used for the fabrication of thin films [6].

These investigations, however, have shown one important fact: if one can overcome the inhomogeneous shrinkage which in general forbids the fabrication of parts, the sintering temperature can be reduced drastically. This should be achievable by homogeneous pore size distribution based on a dense and regular packing.

The question arises now, how far it is possible to utilize this intrinsic properties of nanoparticles for a ceramic processing. The main obstacles as known so far, is the tendency of agglomeration and to overcome the problems well known from sol-gel processing. Ceramic nanocomposites have been emphasized in the past, but for mechanical improvement of ceramics the real broad breakthrough could not be obtained by now. For obtaining nanosized structures in the final product, too much grain growth also has to be avoided.

However, it is difficult to prevent grain growth, since during the sintering process initiated by transport mechanisms in general growth takes place. The homogeneity of green bodies with nanoparticles also seems to be a problem due to agglomeration. This leads to inhomogeneous porous distributions or even bi-mode pore size distributions causing an inhomogeneous sintering process with a total loss of all potential benefits of the nanoscale.

Another serious problem is still the high cost of nanopowders in combination with the described difficulties for processing, which leads to serious obstacles for ceramic nanoparticle utilization.

2 Synthesis of Ceramic Nanoparticles

There are two basic technologies for the fabrication of nanoparticles. The one is the top-down and the other is the bottom-up approach. Top down means milling of large particles or bulk to the nano-size and has been investigated through high energetic milling for example of tungsten carbide. Nanoscale primary particles have been obtained, but the problem of agglomeration cannot be solved by this technique.

However, specific benefits for processing and properties could be obtained by achieving very fine microstructures. Conventional ball milling has been investigated recently with stirred media mills using balls with diameters below 1 mm [7,8]. α-aluminium oxide has been milled into the nanometer size, however, the fraction of arising alumina is too high in order to define this product as nanoscale corundum. In Fig. 1 the different approaches to nanoparticles are schematically shown.

The question arises whether it is possible to overcome the phenomena of recombination during ball milling in order to improve the process obtaining agglomerate-free nanoparti-

cles. For this reason the so called small molecular surface modification concept (SMSM) has been developed [9]. This concept is based on the idea that the recombination time is strongly reduced with decreasing particle size, because the diffusion rate of nanoparticles lays in the range of larger organic molecules, which is fast. However, if very small molecules are used for surface modification and if at the same time they are able to develop strong bonds to the surface, then it should be possible to block the surface before particles aggregate. In Tab. 1, the results of milling experiments utilizing a Drais pearl mill are shown, an ultra sonic generator has been added to the slurry circulation.

Any process leading to nanoparticles (or ceramic colloids) has to be carried out by considering the stability regimes of the suspension according to the rules of colloidal chemistry. These principles are not only valid for milling but also for the synthesis of nanoparticles from molecular dispersions (bottom-up approach) and are basically also valid for sol-gel synthesis. For controlling nucleation and growth, the common rules of course are valid. Nucleation is governed by three thermodynamical parameters, as it is shown in Fig. 2 in equation one.

For the nucleation frequency the free energy of diffusion and the free energy of nucleation (ΔG_N) are important. For the pre-exponential factor, the sigma value (σ_N, interfacial free energy between the nuclear particle and the environment) is important. Nucleation frequency is enhanced by increasing σ_N. The same mechanisms can be used for the growth reactions, where σ_N has values very close to the nucleation.

|	surface modifiers	d_{10} [nm]	d_{50} [nm]	d_{90} [nm]
Alkycarboxylic acids	formic acid	12	17	46
	acetic acid	10	13	27
Ethercarboxylic acids	3-oxabutanic acid	9	12	33
	3,6-dioxaheptanic acid	9	13	24
	3,6,9-trioxadecanic acid	9	11	23
Unsaturated acids	acrylic acid		·	
	methacrylic acid		·	
	sorbic acid		·	
Amino acids	N-(2-hydroxyethyl) ethylendiamine-N,N',N'-triacetic acid	10	13	32
	N-(2-hydroxyethyl)-iminodiacetic acid	9	11,4	13,5
	bicin	8	10	19
	6-aminohexanic acid	11	15	33

Tab. 1
Results of ball milling experiments from zirconia

The free energy for the diffusion does not change. The free energy for nucleation has to be substituted by the value for the free energy for the growth reactions. The important fact is, that by binding molecules to the surface of the nucleus or the growing particle the σ_N can be changed considerably, even to the point that a nucleation or growth reaction can be stopped. With this assumption it should be possible to control particle size and particle size distribution just by appropriate selection of the surface reactive agent as it is indicated in Fig. 2. The effect of a partial surface modification of nanoscaled zirconia by acetyl acetone (ACAC) is shown in part (a) of Fig. 2. Zirconia nanoparticles in aqueous solutions are covered with OH-groups. In reaction with acetyl acetone a surface complex is formed, which clearly can be indicated by the shift of the carbonyl frequency. By blocking a part of the protonically active OH-groupings, the height of the ζ–potential is changed, but not the position of the point of zero charge, because acetyl acetone is not protonically active.
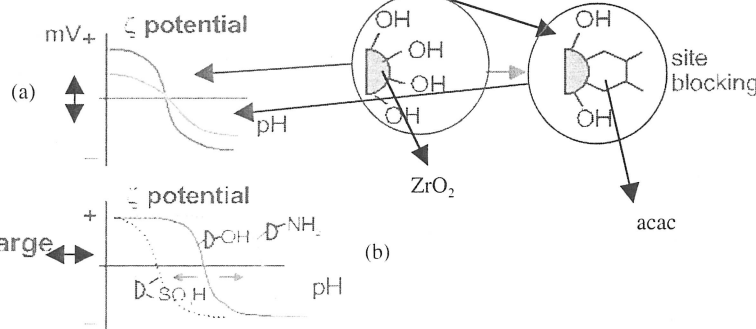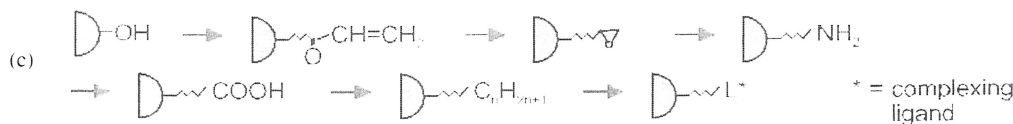
Fig. 2
Principles of colloidal chemistry for synthesis and processing of ceramic nanoparticles

$$I = A \cdot e^{\frac{-(\Delta G_n + \Delta G_D)}{kT}}$$

$$(1) \qquad A = 2n_s \, \upsilon^{1/3} \, \frac{kT}{h} \, \frac{\sigma}{kT}$$

Fig. 3
Control of surface chemistry by surface modification

Steric or/and electrostatic repulsion between the particles
Chemical bonding to the surface by functional groups
(carboxy acids, amines,diketones)Additional functional
groups for the compatibility in the matrix

⇩

zeta potential
surface chemistry
agglomeration
reactivity
compatibilisation

For: i.e.p < 7 amines
   i.e.p > 7 carboxylic acids
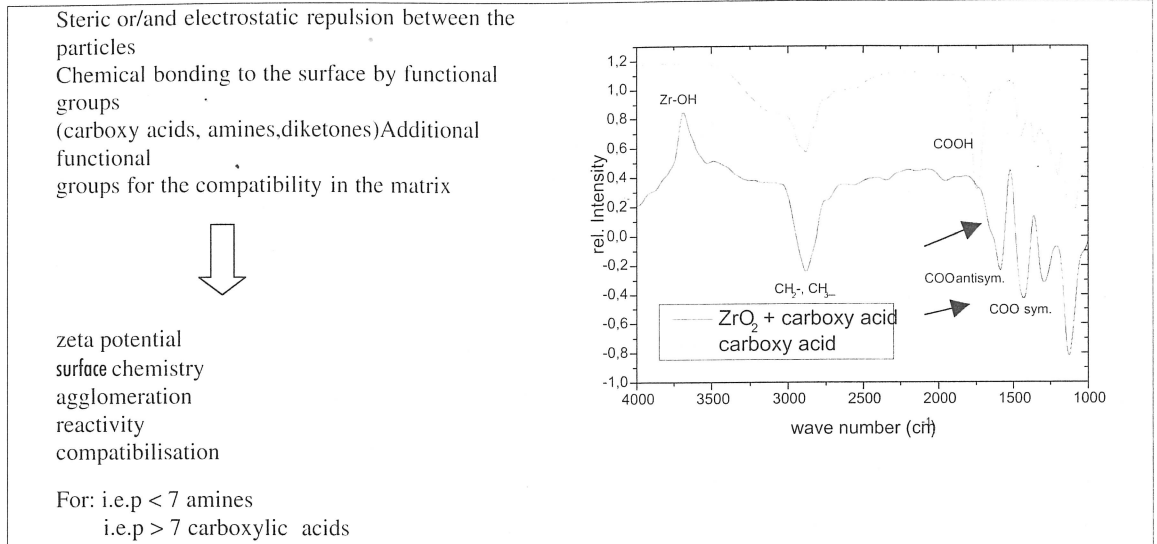
In part (b) of this figure, the surface modification with acetic and basic groupings is shown. This shows that the ζ-potential curve can be shifted considerably within the pH, leading also to a shift of the point of zero charge from the basic to the acid. Moreover, since these groupings are small in size, they do not contribute much to the particle volume and in most cases they can be chosen from organic chemistry, so that they can be burned out very easily if one goes to ceramic processing.

In part (c) of Fig. 2, some examples for surface modification are given and it can be easily concluded, that processing and colloidal stability parameters can be varied in a wide range. For all surface modifiers is common, that they have to form very strong bonds to the surface, for example with silanes or by complex forming or by ionic bonds. Especially if chelating ligants are chosen, which have preferences to specific crystal sites, a shape control during the growth also can be achieved.

The application of these principles for the top down approach through ball milling leads to a process of "milling to the nano size" as already shown in Tab. 1 [10]. The results show, that amongst the chosen surface modifiers, with the exception of the unsaturated organic acids there

are many which lead to a remarkable reduction of particle size down to the nano range.

The best candidates are tri-oxadecanic acid, hydroxy ethylethylenediaminotriacetic acid and bicine, which is an amino acid. For zirconia, acids seem to be by far the best agents. They form very strong bonds to zirconia which is shown in Fig. 3 in the IR spectrum.

The shift of the carboxylic frequency of the free acid to lower wave numbers clearly indicates the formation of a salt-like or a complex type of surface compound. These investigations clearly show, that it is possible to use ball milling for the fabrication of surface modified agglomerate free nanoparticles, since these slurries after drying can be redispersed as well in aqueous as well as in organic solvents, only depending on the type of surface modifier.

The effect of the surface modifier aminosilane (γ-amino propyl triethoxy silane) on the particle size distribution during an ultra sonic supported modification process as shown in Fig. 4 and 5 can be clearly seen. This also shifts the point of zero charge (p.z c.) from pH 4,6 to 8,5.

Fig. 4 (bottom left)
The effect of aminosilanes as surface modifiers on the redispersibility of magnetite

Fig. 5 (bottom right)
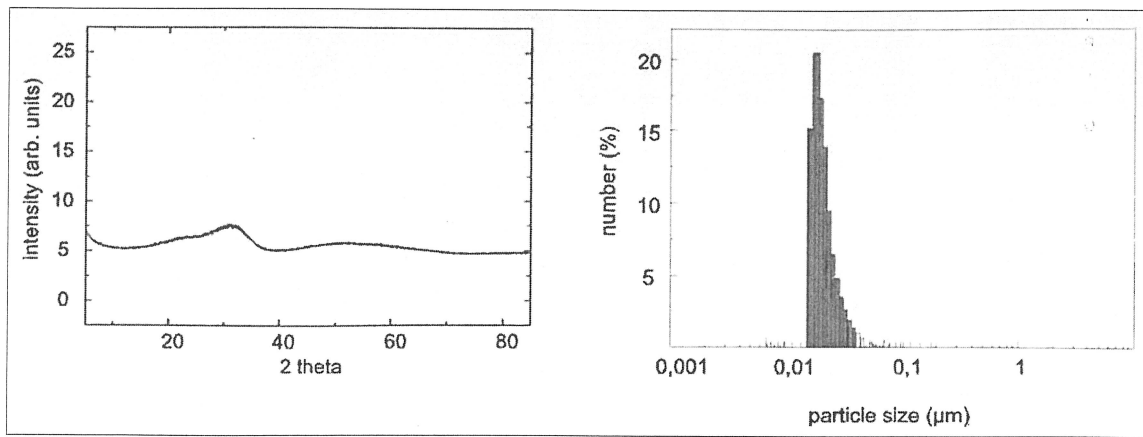HRTEM micrograph of n-magnetite after surface modification
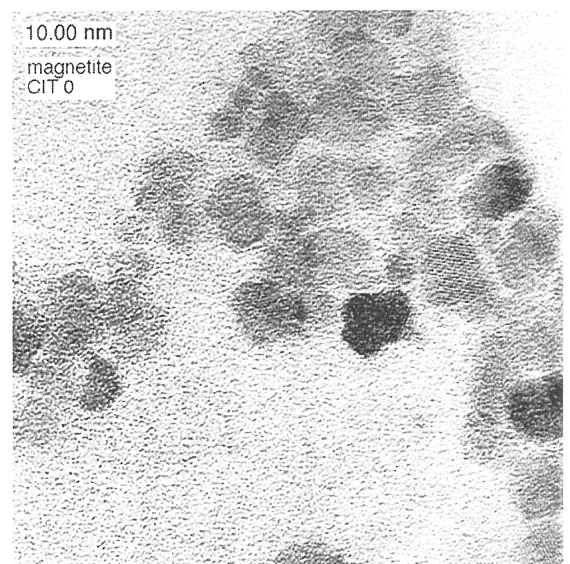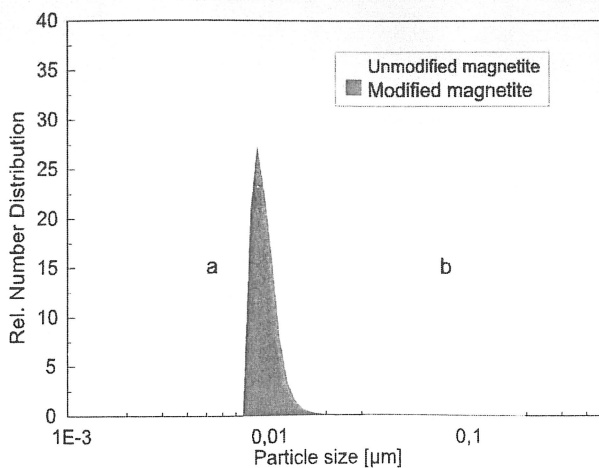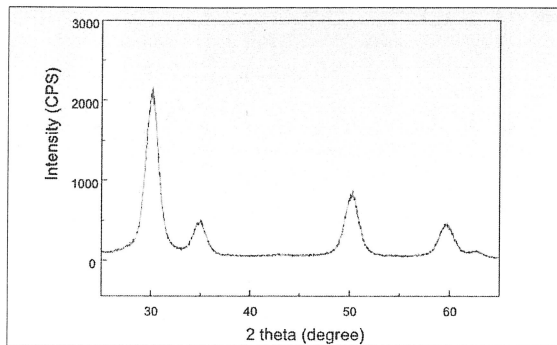
Fig. 7 X-ray diffraction pattern of 6nm ZrO$_2$ after precipitation and hydrothermal treatment
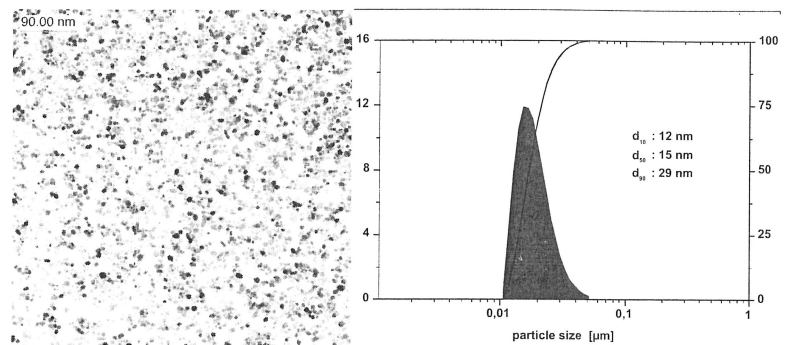
Fig. 8 HRTEM micrograph and particle size distribution of precipitated and hydrothermal treated zirconia

Zirconia, however, if prepared by the controlled precipitation method as explained in Fig. 3 is not crystallized very well. In Fig. 6 and 7, 6...9 nm zirconia X-ray patterns are shown: after precipitation no crystallinity can be detected, whereas hydrothermal treatment leads to fully crystallized zirconia.

In Fig. 8 the micrograph of the redispersed zirconia and the particle size distribution after hydrothermal synthesis and surface modification with trioxodeconic acid is given. As one can see the particles are the agglomerated nano sized distribution.

Utilizing these approaches various agglomerate free nanoparticle systems have been synthesised. Depending on the crystallinity of the precipitate hydrothermal processing is necessary or not, for example in the case of titanium dioxide a newly developed low pressure synthesis (refluxing method) has been developed. Due to the high tendency of TiO$_2$ to crystallize even at lower temperature from solutions, almost no differences between the refluxing and the hydrothermal route can be seen as shown in Fig. 9 and 10.

In summary it is to say that utilizing these approaches, redispersable and agglomerate free nanoparticles with appropriate surface modification can be obtained.

3 Processing and Materials Fabrication

One of the most important facts for material fabrication is the "agglomerate-free" processing to green bodies or composites. The green body consisting of nanoparticulate powders have to own a green density sufficiently high to be sintered to dense parts. Only if the interaction between the particles is low enough, there is a
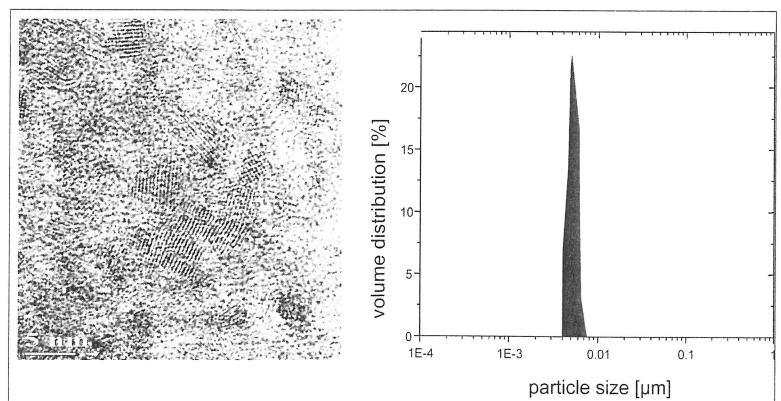

Fig. 9 TEM-micrograph of nano-anatase particles produced by the reflux route and particle distribution
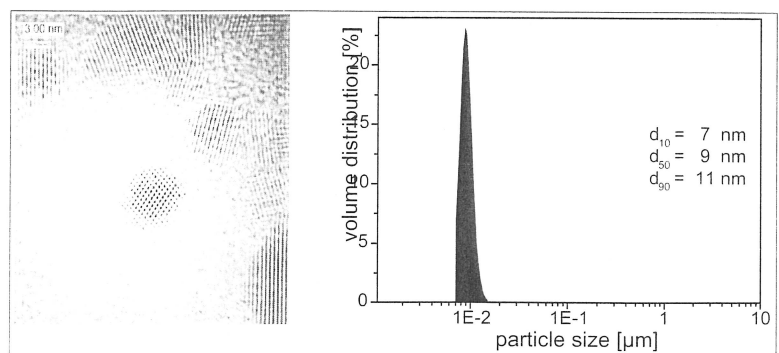

Fig. 10 TEM-micrograph of nano-anatase particles produced by the hydrothermal route and particle distribution

Fig. 11 (left)
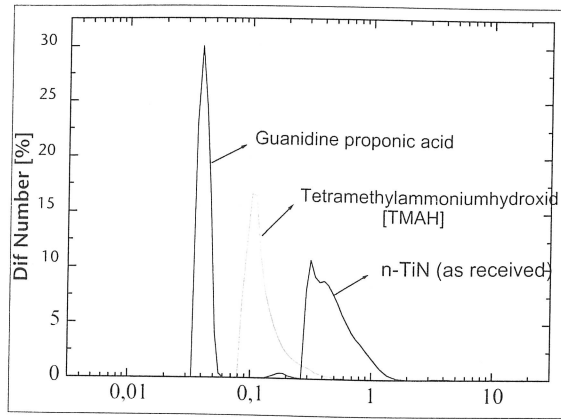Particle size distribution of unmodified and modified TiN

Fig. 12 (right)
Relative density of TiN depending on sintering temperature and sintering atmosphere
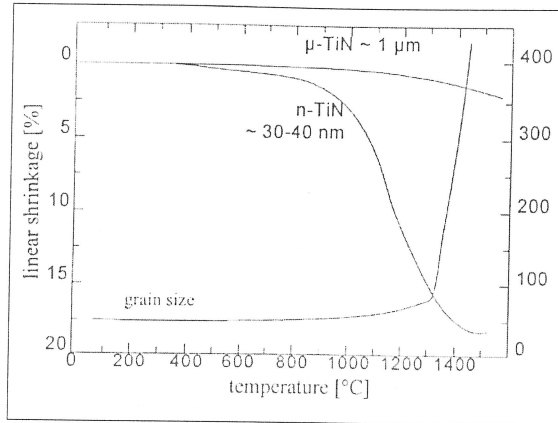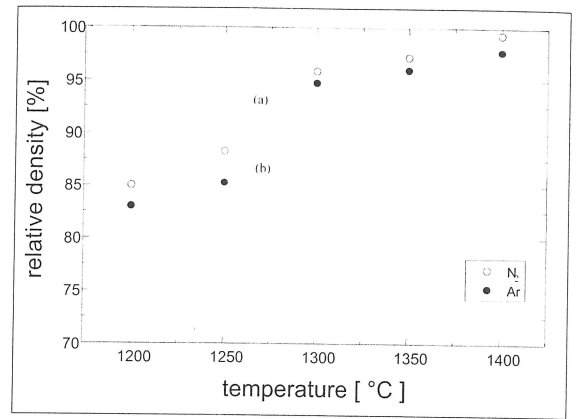

Fig. 13 Linear shrinkage and grain size of TiN depending on sintering temperature

good chance to arrange them closely enough to obtain sufficient green density.

It is well understandable from this consideration that small molecule surface modification is indispensable in order to obtain a sufficiently high ceramic "volume fraction". A too high surface modifier volume, due to the use of polymeric or oligomeric surface modifiers as used in standard fabrication of ceramic slips with submicron particles prevents high solid content systems in the nanosized regime.

Processing experiments with titanium nitride and zirconium dioxide have been carried out in order to realize the sinterability of nanocrystalline green bodies. Titanium nitride has been surface modified with guanodinocarboxylic acid as modifier. Due to this modification well dispersed suspensions can be realized reaching nearly the primary particle size of 40 nm (Fig. 11) leading to homogeneous green bodies.

The green bodies, being produced by casting and pressing the systems to discs [11] could be sintered pressureless to almost theoretical density at temperatures below 1400°C (Fig. 12).

This clearly indicates the great potential of nanoprocessing because it is possible to keep the grain size on the nanoscale for sintering temperatures below 1400°C as shown in Fig. 13.

In the case of zirconia, sintering experiments show, that the sintering temperature of nanoparticulate green bodies can be remarkably reduced. In Fig. 14 the pore size distribution of a cold isostatic pressed zirconia green body and the sintering curve are shown. The particle size is around 9 nm and the surface modifier is trioxadecanic acid.
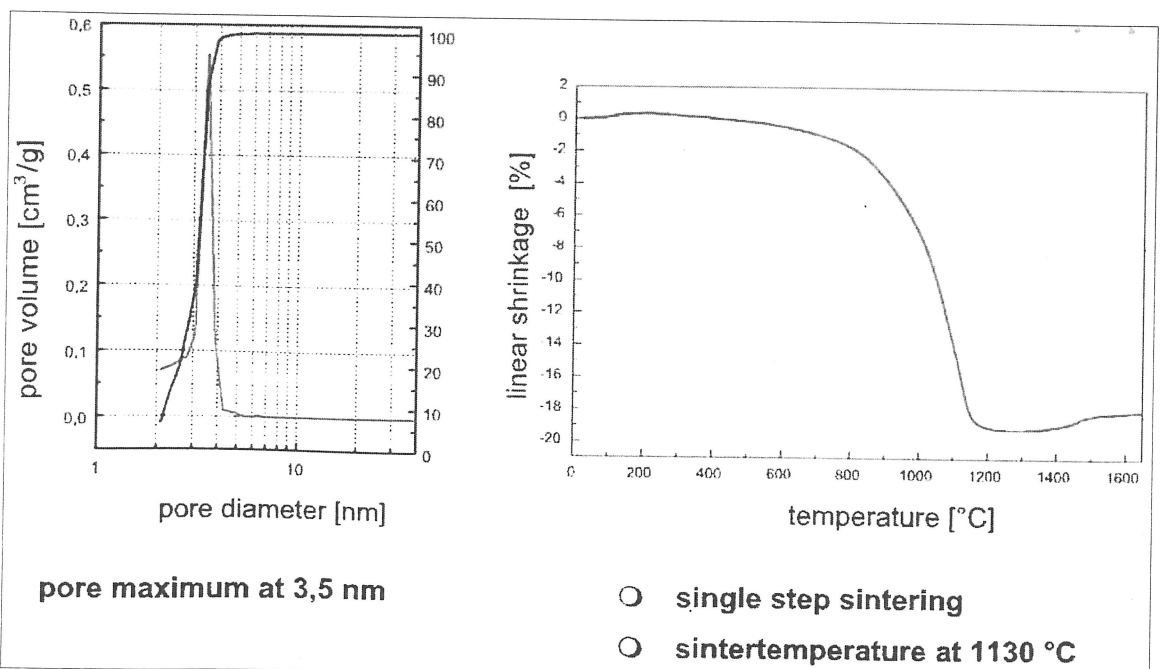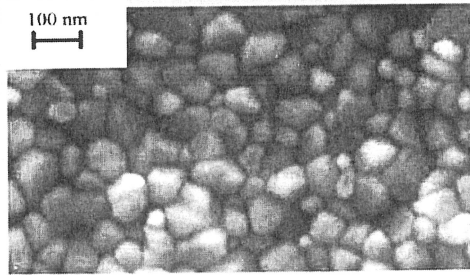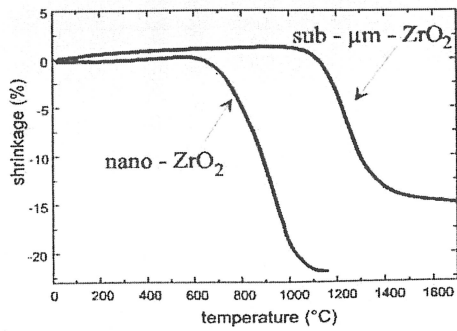
Fig. 14
Pore size distribution and sintering behavior of a green body made from 9 nm zirconia

pore maximum at 3,5 nm

○ single step sintering
○ sintertemperature at 1130 °C

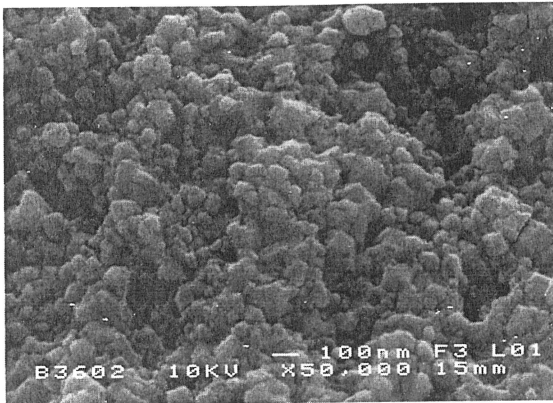**Fig. 15** Comparison of the sintering behavior of sub-μm and nano zirconia

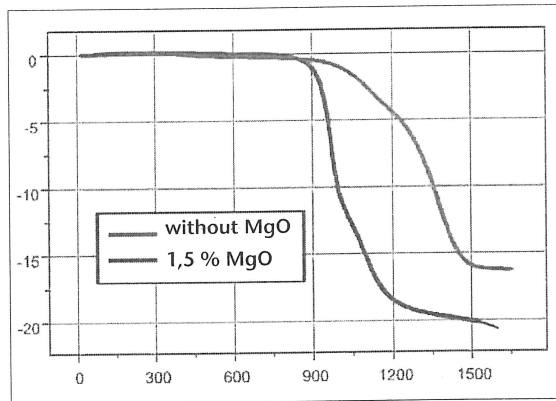**Fig. 16** Sintered microstructure of a green body with 9 nm particles

Fig. 17 Sintering of 50 nm corundum powder; CIP at 800 MPa for 1 min

As one can clearly see there is a mono modal pore size distribution with a maximum at 3,5 nm. This leads to a sintering curve (also shown in Fig. 14), where full density is achieved at around 1130...1180°C. This is just below the phase transition temperature from monoclinic to tetragonal zirconia. Therefore the monoclinic phase is obtained without defect structure due to the phase change. In Fig. 15 an optimized process, based on this powders is shown where the sintering temperature is even lower – around 1000°C – and the micro structure shows a green size below 100 nm and a sinter density of 99 %. This clearly shows the advantages which can be achieved in sintering temperatures by using nanoparticles with homogeneous green structure. As result from surface modification another nanostructured sintered body is shown in Fig. 16.

Similar results have been obtained with corundum with particle sizes of 50 nm as shown in Fig. 17. With 1,5 % magnesia as sinter additive the full density can be obtained at around 1200°C.

High green densities up to 60 % have also been reached by electrophoretic deposition (Fig. 18). These systems can be sintered to completely densified bodies at temperatures of around 1000°C or even less.

Another technology to be developed has been the fabrication of ceramic membranes by lamination technique. Through tape casting (Fig. 19) tapes with organic binders using nano
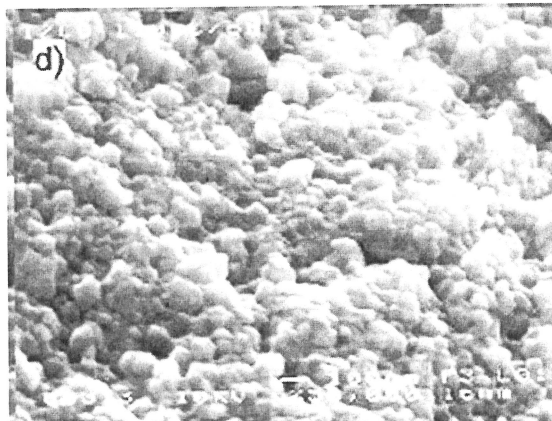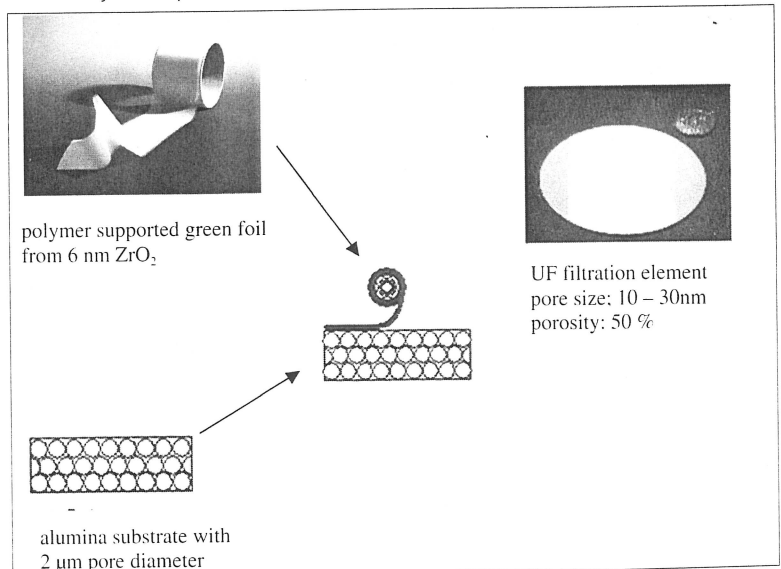

Fig. 18 SEM-micrograph of a sintered nano zirconia body obtained by electrophoretic deposition

Fig. 19 (bottom) Fabrication of ceramic membranes by the lamination technique
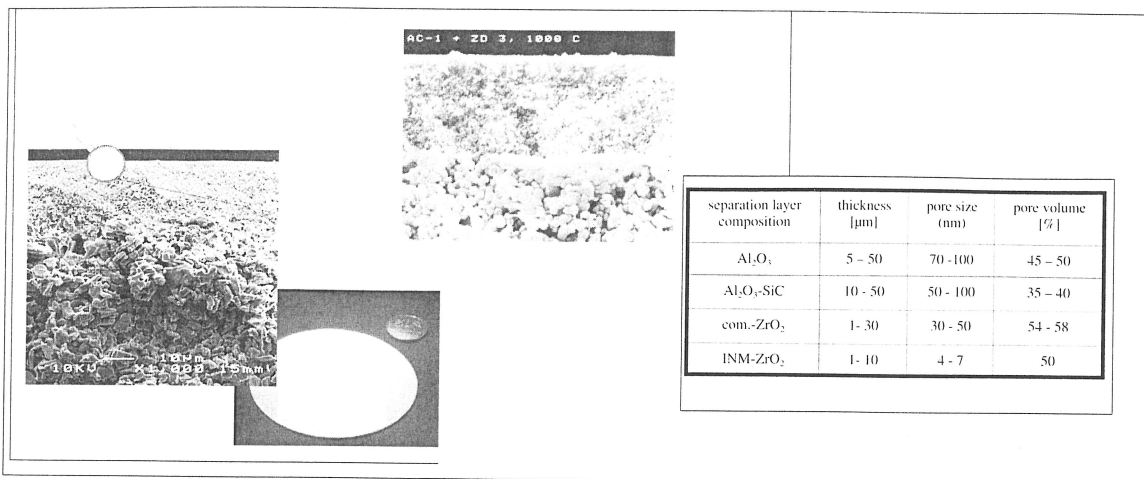

polymer supported green foil from 6 nm ZrO₂

UF filtration element pore size: 10 – 30nm porosity: 50 %

alumina substrate with 2 μm pore diameter

separation layer composition	thickness [μm]	pore size (nm)	pore volume [%]
Al₂O₃	5 – 50	70 -100	45 – 50
Al₂O₃-SiC	10 - 50	50 - 100	35 - 40
com.-ZrO₂	1- 30	30 - 50	54 - 58
INM-ZrO₂	1- 10	4 - 7	50

Fig. 20 Data of supported ceramic membranes fabricated by the nanoparticle lamination technique

Fabrication of very thin ceramic foils (several μm)
• low sintering temperatures
• complex geometries by cutting and punching
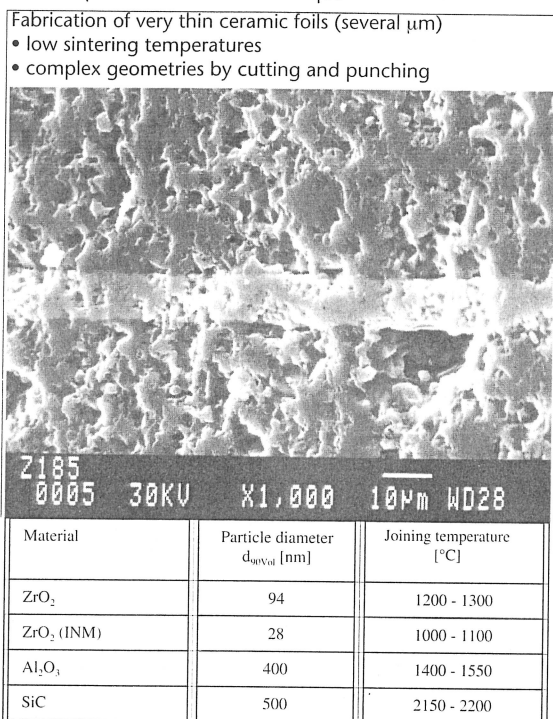
Fig. 21
Ceramic joining with tapes based on nanoparticles

Material	Particle diameter d₉₀Vol [nm]	Joining temperature [°C]
ZrO₂	94	1200 - 1300
ZrO₂ (INM)	28	1000 - 1100
Al₂O₃	400	1400 - 1550
SiC	500	2150 - 2200

Mixing of components by kneading (120°C, 30 min)
Homogenising with high shear rates in a kneader and subsequent granulating
Injection moulding with pressures below 60 MPa at T<135°C
Solvent debinding
Sintering (n-ZrO₂: 1100°C, 1 h)

— 300 μm

Fig. 23
Data of the injection moulding process using nano zirconia

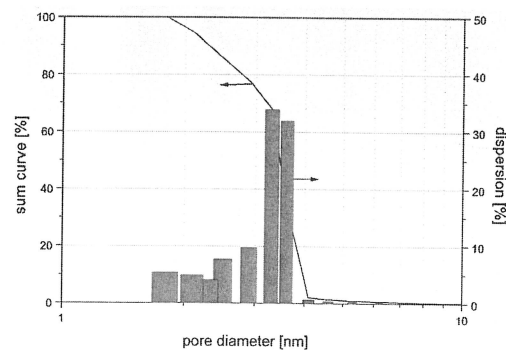| Parameters	INM	State of the art
T [°C]	85 – 130	160 – 220
p [MPa]	30 – 60	60 – 120
Mould temperature	28 – 45	30 – 140

Fig. 22 Pore size distribution of an electrophoretically deposited green body of unstabilized zirconia

zirconia could be prepared on supporting polymeric foils [12]. By laminating the ceramic tapes on top of a ceramic substrate the membranes can be sintered with pore sizes down to the nano meter range.

Fig. 20 shows the basic principle. Surface modified nano zirconia has been dispersed in an organic binder solution and cast on a plastic foil. After drying the flexible tape has been laminated on porous ceramic supports, as shown in Fig. 20.

The Fig. shows the separation layer on top of a porous substrate. Various systems have been used as seen in the Tab. in Fig. 21. The results show, that high porosities in the range of 40...50 Vol.-% and pore sizes down to 4 nm can be obtained. The membranes are extremely flat, because the laminating foil equilibrates the roughness of the porous substrate surface. Another technology, which makes use of the low sintering temperatures is the principle of ceramic foil joining as it is shown in Fig. 22. Various foils have been prepared, which is shown in the Tab. in Fig. 21. Depending on the grain size of the used zirconia, different sintering temperatures have been obtained. Fig. 22 also shows a 10 μm nano zirconia tape joining two alumina parts.

It already has been mentioned that the size is the crucial point for obtaining low sintering temperatures. In Fig. 22 an electrophoretical deposited zirconia is to be seen which also

shows a very interesting pore size distribution with a maximum of about 0,5 nm. With this technique 60 % green density have been obtained.

For the fabrication of ceramic micro parts micrometer powders in general are not suitable due to the large grain size achieved during sintering and inhomogeneous and defects produced in connection with this. Using nanoparticles however, the transport mechanisms through thermal debinding become very slow due to the extremely small poor size. So the danger of building up pressure in the part causing defects is very high.

For this reason a specific binder system has been developed for solvent debinding, which consists of a small fraction of an insoluble polymer for providing sufficient green density and solvent extractable binders for a "soft" debinding. In Fig. 23 the results including description of the process and the processing parameters as well as a moulded gear wheel are shown.

Film patterns of ceramic materials applied by screen printing are important in the field of electronics and sensor applications. Utilizing this technology in combination with nanoparticles offers the possibility to produce patterns characterised by very fine line widths and thicknesses in the lower micrometer range at low sintering temperatures. Especially in the case of sensor applications the high specific surface area of these particles permits an increase of sensitivity and time of response.

Fig. 24 shows the basic principle and an example of a coated sensor. Pastes basing on surface modified nanoparticles dispersed in an organic binder solution are forced through stencil screens onto the substrates using squeegees. Multi layer structures are producible with high reproducibility without firing after each application step in high precision and small dimensions.

Using this technology, defect free small parts down to the micrometer range will be possible. Colloidal chemistry in connection with ceramic technologies also can be used for the fabrication of high grade ceramic powders. It is a well known problem, that the homogeneity of ceramic powders, especially if dopants or sinter additives have been used in small fractions, showing different chemical or physical properties (for example large differences in density), lead to inhomogeneity by segregation effects as a consequence to an inhomogeneous distribution of dopant or additives in the green body. This, in general, leads to the deformation by tensions and it is very difficult to produce exactly dimensioned parts, especially if large parts are taken into consideration. For this reason, the technology for immobilizing dopants and additives by colloidal techniques on top of ceramic
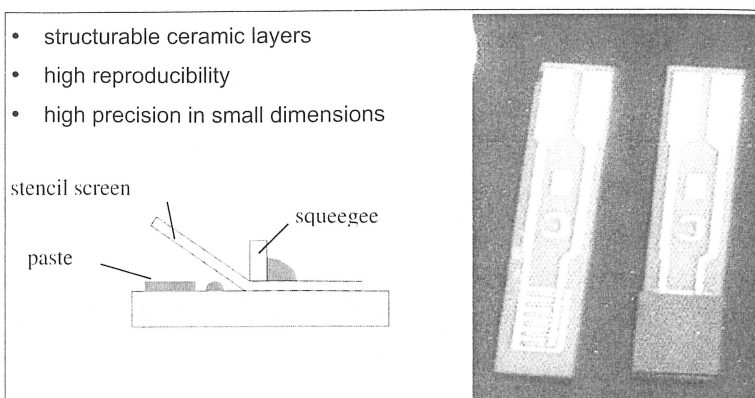
- structurable ceramic layers
- high reproducibility
- high precision in small dimensions

stencil screen

squeegee

paste

Fig. 24
Fabrication of ceramic patterns by screen printing and sensor with ceramic coating

powders has been developed as shown elsewhere [13]. Using carbon black on the top of SiC is an easy process for the fabrication of high grade large parts, for example such as burners or other parts as shown in Fig. 25.

Using this approach, very fine grained SiC can be processed to parts. Due to the homogeneous distribution of the carbon black, the SiO_2 content in the grain boundary could be reduced to a level that doping with nitrogen does not lead to a loss of nitrogen even at high temperatures and the conductivity based on the nitrogen doping does not change by time. This has been used for the fabrication of high performance igniters.

In addition nanoscaled particles in combination with hydrolysable silanes can be used as porous
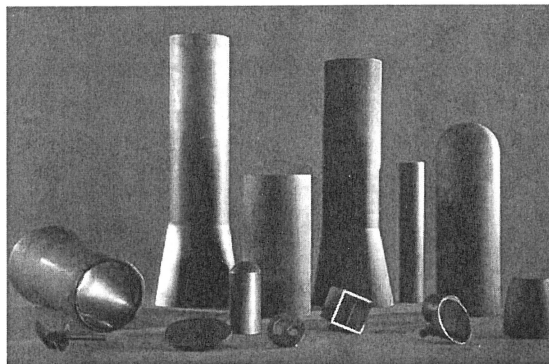

Fig. 25
SiC parts utilizing colloidal chemistry route for homogeneous distribution of the carbon black on SiC
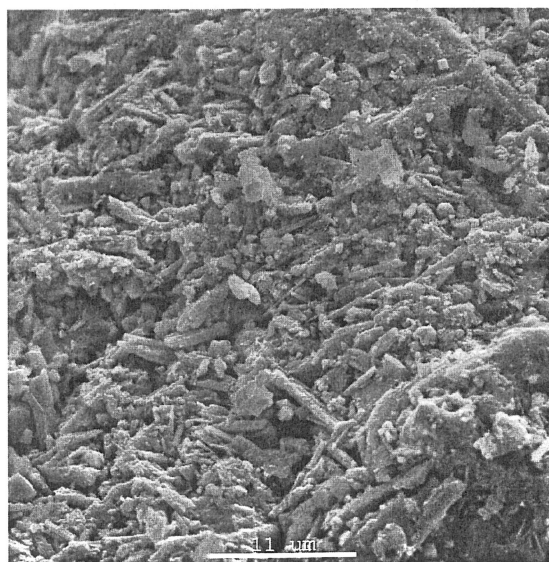

Fig. 26
Oxidation catalyst coating containing a mixture of different particles and a sol-gel-binder after thermal treatment at 400°C

binder systems with good mechanical properties and high specific surfaces (50...500 m^2/g) caused by micro pores (< 2 nm). The pore size distribution can be tailored by thermal treatment and the choice of silanes.

These binder systems allow the manufacturing of catalytically active materials, e.g. coatings with non-specific oxidation catalysts for the degradation of volatile organic components (VOC) at temperatures above 250°C on various substrates (glass, ceramics, metals) by standard techniques like spraying, dipping and flow coating. Porous layers with good adhesion and high catalytic activity are obtained after thermal curing. The choice of the active components (e.g. mixtures of transition metal oxides) enables the adjustment of activity and selectivity for the respective process. Fig. 26 shows a SEM-micrograph of a catalytic coating after thermal treatment at 400°C.

4 Compounds

Nanoparticulate ceramic systems also have a great potential for the fabrication of polymer matrix nanocomposites. These composites are defined by the ceramic particle to polymer matrix interface which forms a new interfacial face. As experiments have shown [14], the effect only is remarkable if the particle size of the ceramic nanoparticles is in the lower nanometer range at around 10 nm. Then, however, the storage modules and the Tg can be changed remarkably. For example in PMMA the Tg can be increased from 110 to 140°C. Other parameters to be influenced are the abrasion resistance of the polymer, while remaining transparent, but also the gas diffusion. These composites can be obtained by mould compounding, using surface modified nanoparticles which provide a compatibility to the polymer matrix.

5 Conclusion

The use of ceramic nanoparticles is at its infancy. The drawbacks are still the high costs of the nanoparticles. For this reason, the fabrication technologies have to be improved, but the crucial point is the aggregation governed by the surface chemistry. The surface chemistry utilizing known chemistry and inorganic colloidal principles are the basis for a appropriate processing, however if this is carried out, interesting new processing routes can be developed for ceramics, ceramic coatings, but also for compound technologies.

References

[1] H. Gleiter: "Nanocrystalline Materials", Pergamon Press, Oxford (1989)
[2] A. Henglein: "Mechanisms of reactions on colloidal micro-electrodes and size quantization effects", Topics in Current Chemistry **143** (1988) 113–180
[3] H. Weller: " Quantized Semiconductor Particles: A Novel State of Matter for Materials Science", Adv. Materials **5** (1993) 88-95
[4] M. Mennig, M. Schmitt, U. Becker, G. Jung und H. Schmidt: "Gold colloids in sol-gel derived SiO$_2$ coatings on glass and their linear and nonlinear optical properties", SPIE 2288 (1994) Sol-Gel Optics III 130–139
[5] O. Stern: Zeitschrift Elektrochemie, 508 ff (1924)
[6] C. J. Brinker, G. W. Scherer: "Sol-gel science: the physics and chemistry of sol-gel processing", Academic Press, Boston (1990)
[7] S. Mende, F. Stenger, W. Peukert, J. Schwedes, "Mechanische Erzeugung und Stabilisierung von Nanopartikeln in Rührwerkskugelmühlen", Chemie Ingenieur Technik **74** (2002) 994-1000
[8] F. Tabellion, H. Schmidt: "Chemomechanisches Verfahren und Herstellung von Funktionskolloiden in Rührwerkskugelmühlen", Chemie Ingenieur Technik **75** (2003) 1134
[9] H. K.Schmidt: "Kona powder and particles" **14** (1996) 92-103
[10] H. Schmidt , F. Tabellion, K.P. Schmitt, P.W. Oliveira: "Ceramic Nanoparticle Technologies for Ceramics and Composites", Ceramic Transaction, in press
[11] R. Nass, S. Albayrak, M. Aslan, H. Schmidt: "Colloidal Processing and Sintering of Nanoscaled TiN", Ceramic Transactions: Ceramic Processing Science and Technology, Am.Ceram.Soc. **51** (1995) 591-595
[12] Dissertation, B. Walter: "Beschichten poröser Träger mit nanoskaligen, keramischen Folien für Ultrafiltrationsanwendungen", Universität Saarbrücken (1999)
[13] M. Aslan; J. Spehr; R. Naß; H. Schmidt; P. Matje: "Herstellung großvolumiger SiC-Bauteile über kolloidale Formgebungsverfahren", Werkstoffwoche 1996; Werkstoff- und Verfahrenstechnik, Symp. 6, Stuttgart 28.-31. Mai 1996 6 (1997) 543-549
[14] Dissertation, C. Becker: "Struktur-Eigenschafts-Beziehungen in thermoplastischen Nanokompositen an polymethacrylat-basierten Modellsystemen", Universität Saarbrücken (1998)