Relevance of Sol-Gel Methods for Synthesis of Fine Particles †

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Abstract

Sol-gel techniques are interesting for the synthesis and processing of fine particles if the problems of stabilization of colloidal particles, their agglomeration and the fabrication of green bodies with high density are solved. A new approach for the fine particle fabrication from solution was realized by controlling nucleation, growth and surface reactivity by surface modification through selected organic molecules. A variety of nanopowders (e.g. ZrO_2, Al_2O_3, PZT) have been synthesized, and a scaling-up process has been established. Ceramic green bodies show substantially reduced sintering temperatures.

1. Introduction

Synthesis and processing of ceramic or metallic powders is a very interesting direction with respect to the fabrication of new materials or the improvement of ones already in existence [1]. Inorganic particulate materials are mainly produced in two ways: one is the use of natural raw materials such as quartz, $CaCO_3$ or $CaSO_4$. The other way is to produce them by synthetic processes involving chemistry in the most cases. Examples for this are $BaTiO_3$, Al_2O_3 or SiC. The powders are used for various purposes such as pigments for lacquers, raw materials for ceramics or as fillers for polymers. Most of the powders obtained from grinding processes possess particle sizes in the micrometer range. To gain smaller particle sizes in the nanometer range, for example, special techniques such as flame pyrolysis (for SiO_2 or TiO_2), which is an important technical process, are required. Other techniques such as evaporation and condensation through vapor phases [2], laser pyrolysis, plasma pyrolysis or others are in their infancy. There is an interesting potential connected to very small particle technologies such as very low sintering temperatures and the homogeneous introduction of additives to ceramic powders, for example. In order to exploit the potential of nanoscaled particles, it is necessary to develop appropriate production techniques which are able to fulfill the quality requirements for powders, especially the

prevention of agglomeration. The second important problem to be solved is the processing, which means it is necessary to develop methods to process nanoscaled particles into parts.

Similar ideas have been investigated in connection with sol-gel techniques using so-called sols as intermediates [3, 4]. Inorganic sols consist of nanosized particles suspended in aqueous or non-aqueous solutions stabilized by electrostatic forces. Surface charges obtained by adsorption of OH-groups or protons to the particle's surface prevent the agglomeration. The destabilization of these sols leads to gels with very low solids contents, so that this method is not suitable for ceramic parts fabrication. For these reasons, it was doubted that it is possible to use sol-gel techniques successfully for ceramic parts production (**Figure 1**).
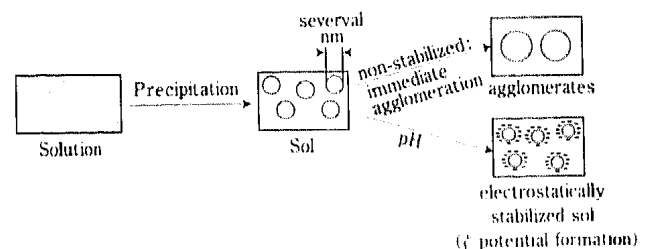

Fig. 1 Schematic of the sol-gel process as colloidal route based on electrostatic stabilization.

Based on this state of the art, investigations were carried out to overcome the problems of electrostatic stabilization by controlling the surface of the small particles by chemical means, first during the synthesis and secondly for processing. In this paper, a summary is given on the possibilities of fabrication and processing of ceramic fine powders and how to process them to materials.

2. General principles

In this chapter, chemical principles for the control synthesis of small particles are described. As it is well known, it is possible to precipitate a variety of materials from solutions. In this case, a nucleation step is necessary to initiate the process. The nucleation rate depends on the free energy of the nucleation step (for overcoming the critical radius for nucleation) and the free energy for the diffusion, which is a function of the temperature, liquid and size of the dissolved components to be deposited. The nucleation rate can be expressed by equation (1) and (2) [5-7].

$$I = A \cdot e^{\dfrac{-(\Delta G_n + \Delta G_D)}{kT}} \qquad (1)$$

$$A = 2n_v \cdot v^{1/3} \frac{kT}{h} \sqrt{\frac{\sigma}{kT}} \qquad (2)$$

ΔG_n: Gibbs free energy for nucleation
ΔG_D: Gibbs free energy for diffusion
n_v: number of nucleating or crystallizing species per unit volume of the liquid
v: volume per formula unit of the nucleating species
σ: interfacial free energy

These equations, of course, are also valid for the growth of particles after the nucleation has taken place, if ΔG_n is replaced by ΔG_c (Gibbs free energy of condensation or crystallisation). In this case, the surface free energy σ of the growing particle becomes extremely important. These equations do not give any information about mono or polydispersity. To control the dispersity, assumptions have to be made about the interaction of surface active additives. It is assumed that each molecule requires a well defined area for optimal binding. This leads to an energy minimum at a well defined surface coverage and the total surface area of the system then will be controlled by the space requirement of the ligands. Assuming further that the growing system tends to form parti-

cles as large as possible, a minimum of the surface free energy should be obtained at a monodispersed particle size with total surface area corresponding to a complete coverage of the formed particles. This was calculated by Strehlow [8] for a Stöber system [9] and could also be experimentally shown with various surface modified systems where particle sizes could be obtained in process techniques not controlling nucleation and growth by La Mer's model [10]. In the optimal case, the Gibbs free energy of the system reaches its minimum in a monodispersed state, as described elsewhere [11]. In order to influence the surface free energy, additives with affinity to the growing particles' surface were used such as complex formers, acids and bases, surfactants or reactive silanes or components reacting to the surface (Figure 2).

Depending on the type of reaction, the growth process can be stopped or continued with different rates. The most interesting reaction type is one which does not stop the growth process but prevents agglomeration. This can be obtained by choosing the appropriate molecule to be bounded or adsorbed to the surface. Functional molecules with the second function can be used to obtain specific surface reactivities for a variety of purposes. If the second function is an inert function (e.g. the alkyl group of carboxylic acids), the interaction between particles is controlled by Van der Waals forces only. Van der Waals forces are weak compared to chemical bonds (ionic or covalent). In very small particles, these types of bonds are present in a rather high concentration per volume unit due to the high surface area and, in general, lead to irreversible agglomeration. The "reduction" to van der Waals forces as the dominating force, however, leads to easy redispersion in suitable liquids even after drying and allows a
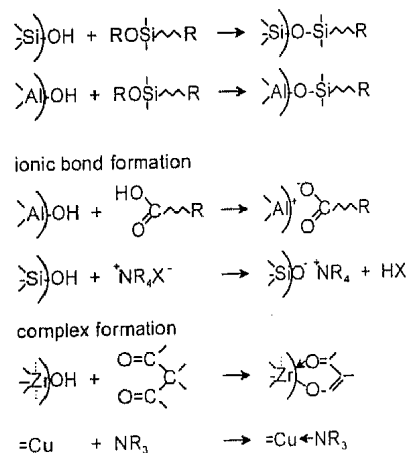
Fig. 2 Examples of surface modification principles with different types of chemical bonds.

dense packing with nano particle systems in green bodies, not obtainable with surface modification [12]. In the case of boehmite with 15 nm particle size, green bodies with densities up to 60% by volume were obtained after drying. This is not possible with electrostatically stabilized sols (gel solids content of 10−20%).

Based on these considerations, a thermodynamical model was developed [11] which postulates that by the appropriate choice and concentration of surface modifiers during a nucleation and growth process, the particle size and particle reactivities can be tailored. In **Figure 3**, an example is shown using zirconia propylate reacted with acetyl acetone and hydrolyzed by water addition. The precipitate "formed" by hydrolysis and condensation is nanoscale, and the particle size depends strongly on the concentration of the ß-diketone. As could be shown clearly, the ß-diketone concentration dependence of the particle size follows a reciprocal function ($y = K \cdot 1/x$). The particle diameter is rather uniform ($\approx \pm 1$ nm).

This type of reaction is called controlled growth process (CGP) and can be used for nanoparticle production for single-component systems or multi-component systems, if the nucleation and growth process of the different components is similar under the desired thermodynamical parameters.

Other examples using the interfacial free energy as a tool are microemulsion systems [12, 13, 14]. In this case, the interfacial free energy is decreased to a level such that the emulsified state becomes
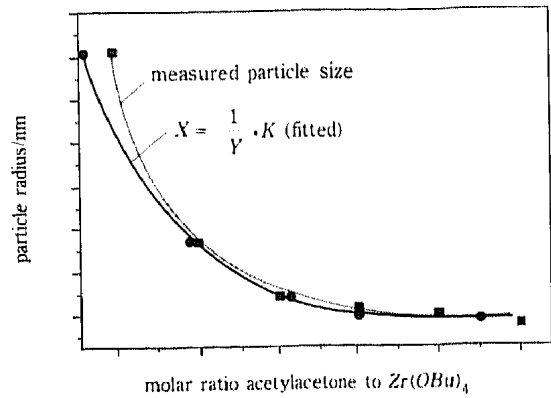
Fig. 3 Dependence of zirconia particle sizes as a function of the complex former concentration; complex former: acetyl acetone.

stable. For this reason, ionic surfactants are generally used. However, ionic surfactants are very sensitive to the ion strength of the aqueous phase, which, in general, should be the dispersed phase in order to obtain particles by precipitation and from sol solutions. In order to avoid these complications, systems consisting of non-ionic surfactants have been built up [15], and it was possible to demonstrate that stable microemulsions could be obtained, the stability of which is independent of the dissolved salts. The flow chart of this process is shown in **Figures 4** and **5**.

The droplet size of the microemulsion can be adjusted by altering the ratio between the oil phase and the water phase as well as the type and concentration
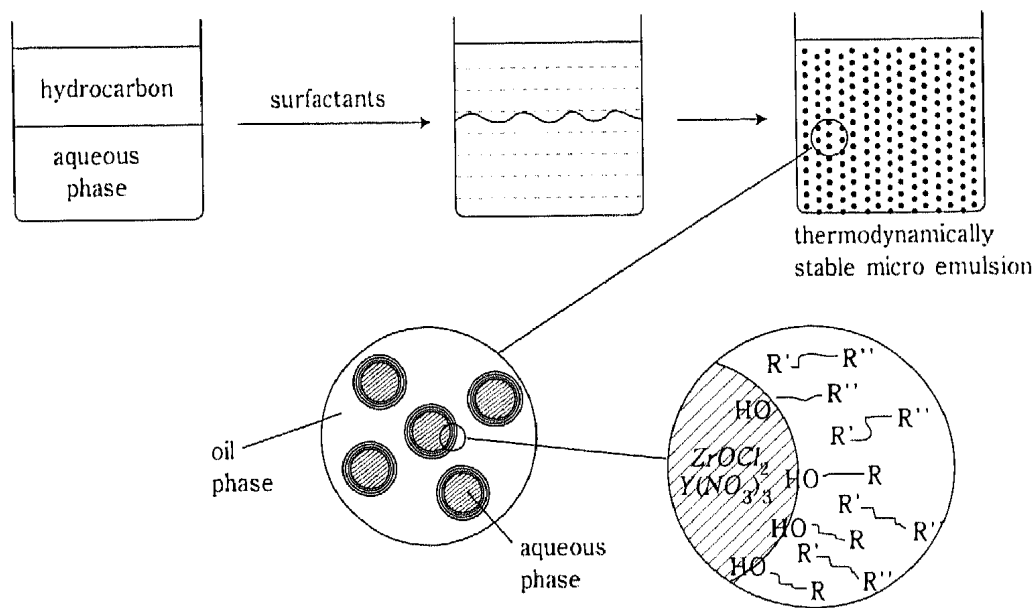
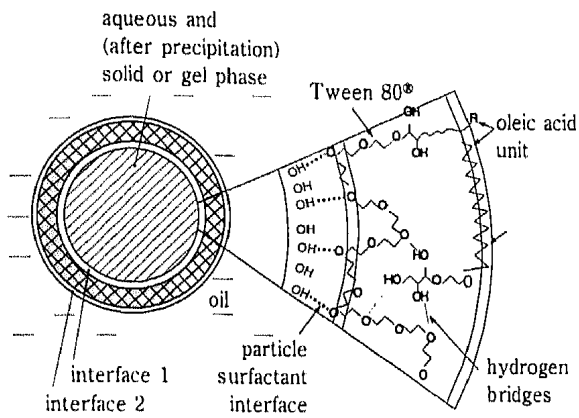**Fig. 4** Principles for the preparation of a microemulsion with Y/Zr.

Fig. 5 Structure of the thermodynamically stable water-in-oil microemulsion.

of the surfactants. The stability of the emulsion ends at the so-called inversion point where the water-in-oil emulsion switches to an oil-in-water emulsion. As shown by Burgard [16] with non-ionic tensides, micro-

emulsions can be stabilized in an up to 45% aqueous phase. The solid particle formation now takes place by adjusting a pH value within the droplets to precipitate the particles. In the zirconia-yttria system, base pH has to be chosen. This can either be obtained by introducing ammonia into the system or by ion exchange with basic ion exchangers and a charge transfer catalyst, for example, quarternaire ammonium bases which transport OH groups into the system. In **Figure 6**, the process routes of the microemulsion and the CGP route are compared.

The volume yield of MEP is remarkably lower, but is a more general route since it is not limited to a few components having similar growth properties. The CGP process has meanwhile been converted to a pilot-scale continuous-flow process with 1−2 kg yield powder per hour. The described principles have been used for the fabrication of a variety of powders such as zirconia, yttria-stabilized zirconia, bariumtitanate, PZT or alumina.
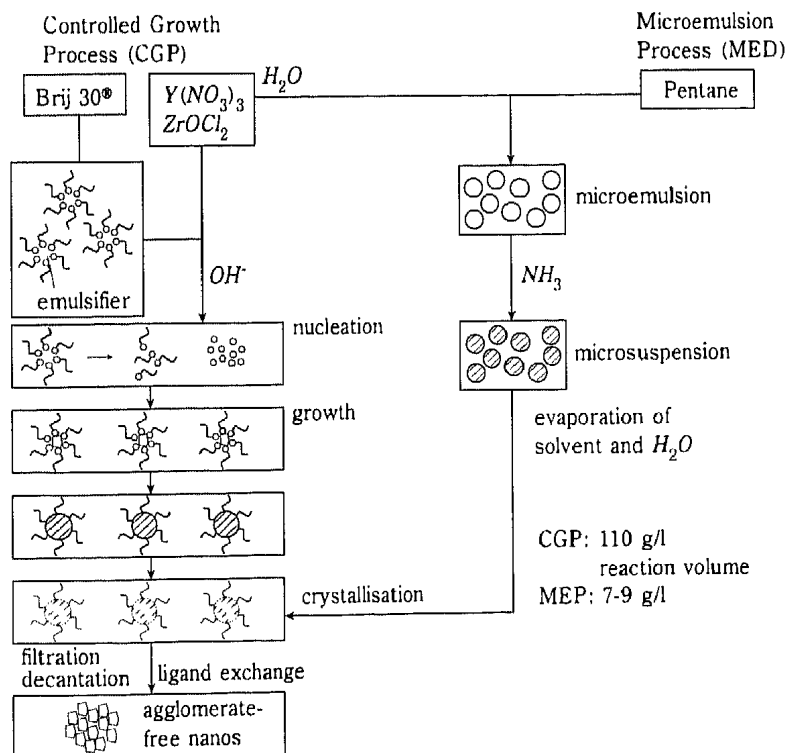

Fig. 6 Comparison of the CGP with the MEP process and obtainable volume yields.

3. Powder Calcination

To obtain well-defined powders, however, the systems have to be crystallized in most cases. In **Figures 7** and **8**, the cleaning and crystallization process of $5Y-ZrO_2$ is shown [16]. The cleaning of the nano slurry was carried out by dialysis and the crystallization by hydro-thermal treatment in the presence of ß-diketones as surface modifiers.

In **Figures 9, 10** and **11** [17], several other nano-scale powders produced by the CGP process are shown. As one can see, the powders are either not agglomerated at all or only to a very low degree. In each case, the powders can be redispersed in organic or even aqueous solutions very easily.

Figure 12a shows the $5Y-ZrO_2$ and **12b** the HRTEM image. It shows that the particles are well crystallized.

Another route has been employed in the case of boehmite. Heavily agglomerated boehmite powder as available from industry can be redispersed by re-fluxing the system for 10 or more hours in acedic or propionic acid [18, 19, 20]. During this process, necks formed between different boehmite crystal-
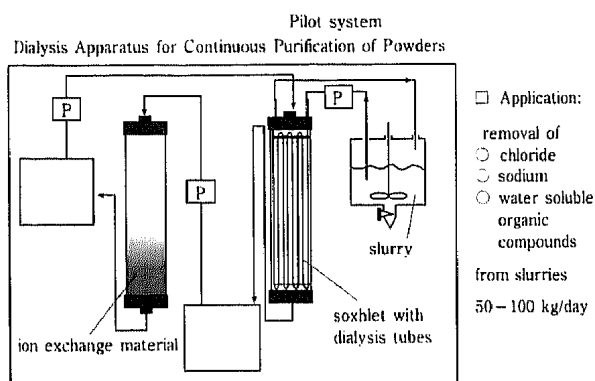

Fig. 9 TEM micrograph of SnO_2 produced by the CGP process.
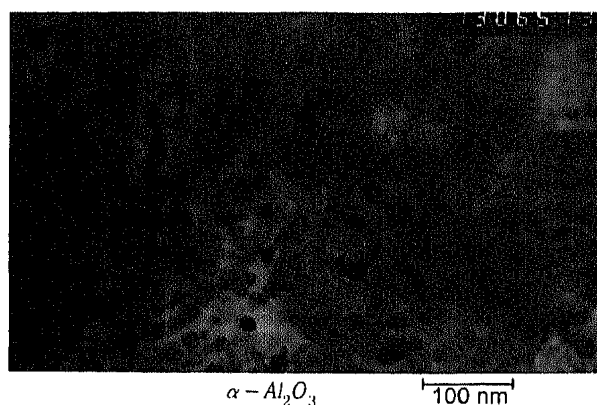
Fig. 10 TEM micrograph of $\alpha-Al_2O_3$ produced by the CGP process.

Pilot system
Dialysis Apparatus for Continuous Purification of Powders

☐ Application:

removal of
○ chloride
○ sodium
○ water soluble organic compounds

from slurries

50 – 100 kg/day

Fig. 7 Flow chart of the cleaning process. S = storage container for the extraction liquid; P = pumps.

Continuous flow hydrothermal reactor

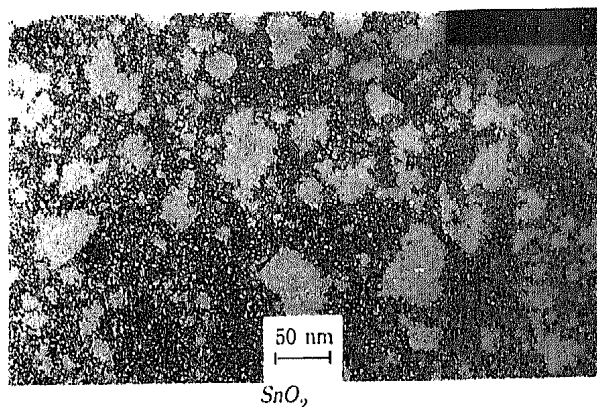

Inertgas

1. pump
2. heataer
3. reactor
4. security valve
5. valve
6. pressure gauge
7. temperature control
8. cooler
9. storage tank

Fig. 8 Flow chart of the hydrothermal crystallization.

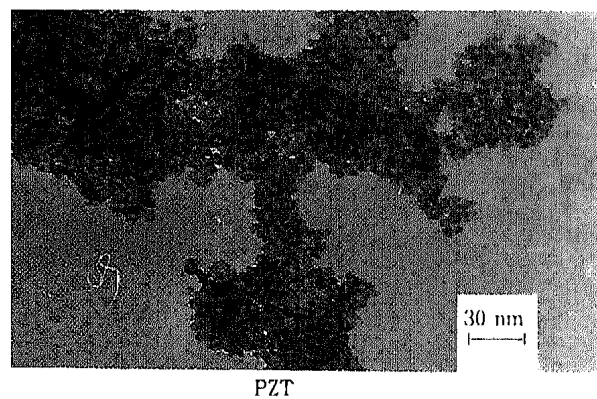**Fig. 11** TEM micrograph of PZT powder produced by the CGP process.

lites caused by condensation can be dissolved. The deagglomerated particles are shown in **Figure 13**.

After dissolving the necks, the suspension can be filtered using nanofiltration or dialysis, resulting in viscous pastes. These pastes can be redispersed in aqueous or organic solvents such as alcohols. Surface analysis of the dried pastes by DRIFT (**Figure 14**) spectroscopy shows that the boehmite still contains about 3 wt.-% of propionic or acedic acid, which
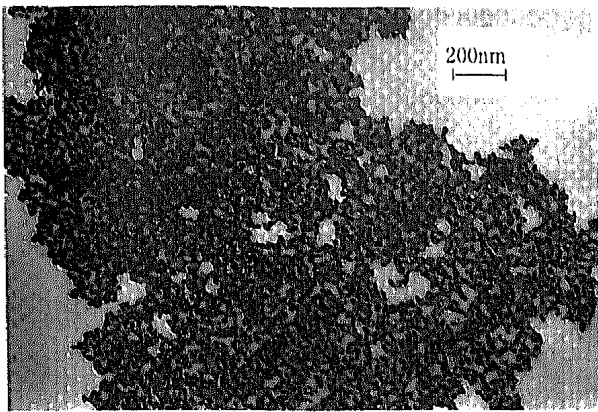
Fig. 12a Electron microscopic images of 5Y-ZrO$_2$.

Fig. 12b Electron microscopic images of 5Y-ZrO$_2$.
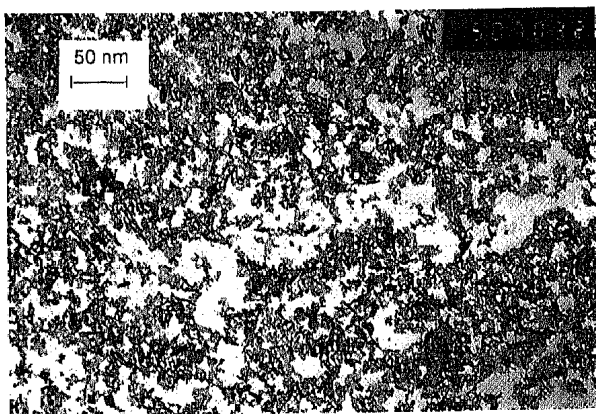

Fig. 13 TEM micrograph of 15 nm boehmite after deagglomeration.

cannot be washed out.

The increase of the solids content in comparison to electrostatically stabilized AlOOH sols does not lead to a gel point, but slowly increases the viscosity. At a solids content of about 40 to 45 vol.-%, the system forms extrudable pastes. At solids contents of about 30% by volume, slips can be formed. Extrusion of these pastes simplified by the addition of about 1 or 2 wt.-% of polyvinyl alcohol leads to shaped bodies such as tubes with solids contents up to 60% by volume after drying. This is an extraordinarily high value which has never been obtained by the simple sol-gel process. This leads to the conclusion that sol-gel techniques, despite many opinions to the contrary, will gain a new potential for ceramic processing. The drawback of sol-gel processes as discussed in the years around 1985 was that sols showed too low solids contents for ceramic parts fabrication since it was only electrostatic stabilization that was used. But with gels of 60% by volume solids contents, ceramic firing with "normal" shrinkage rates can be obtained. Of course, boehmite is not a suitable system for the processing of aluminum oxide parts, but based on these findings, a membrane fabrication process has been developed.

Due to the fact that these nanoparticles can be obtained by rather simple precipitation processes, the costs of these powders are in the range of conventional sub-μm powders. There is still a great potential for simplifying the synthesis technique by scaling-up using the rules of chemical engineering.

4. Processing of Nano-Scale Particles

As shown in the previous chapter, it is possible by appropriate surface modification to obtain redispersible nano-scale ceramic powders. In order to process these powders, several important factors have to be considered. One of the interesting potentials of processing nano-scale powders is the option of very low sintering temperatures which can be calculated from the particle radius (calculations for α-alumina, for example, result in the requirement of having particle sizes below 30 nm to obtain sintering temperatures below 1000°C). Another option is to produce defect-reduced ceramics. This will only be the case if the grain growth during the densification process remains low. In this case, a new strategy for the fabrication of ceramic parts will become possible: to densify the ceramic part without the formation of large defects due to pore formation or large grain formation, and then in a second step to increase the grain growth and to form the desired
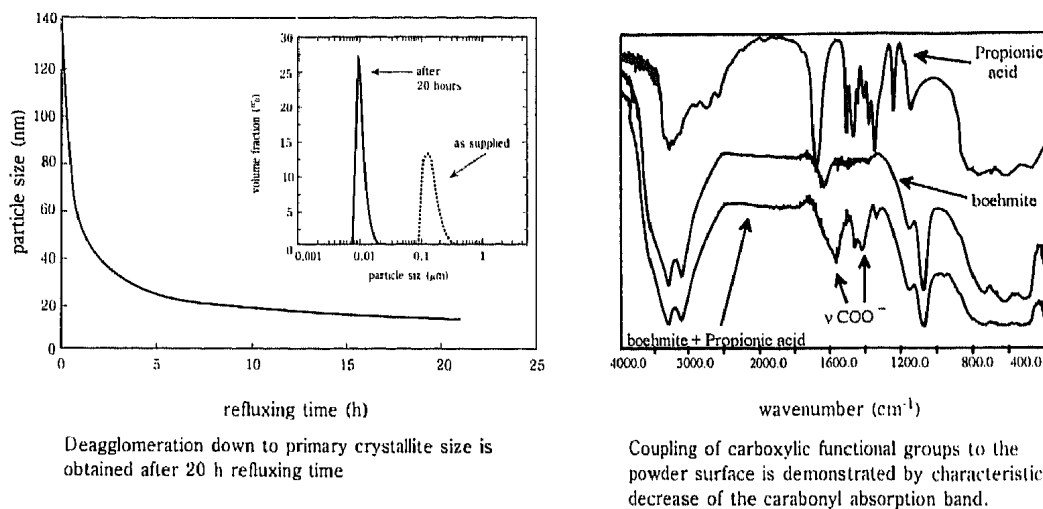
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Deagglomeration down to primary crystallite size is obtained after 20 h refluxing time

Coupling of carboxylic functional groups to the powder surface is demonstrated by characteristic decrease of the carabonyl absorption band.

Fig. 14 Effect of deagglomeration of boehmite using proprionic acid and IR spectra of free and adsorbed propionic acid.

microstructure. For low-temperature sintering as well as for defect-free processing, it is necessary that the green body shows a homogeneous pore size, preferably in the lower nano range. In order to keep shrinkage to a tolerable level, a homogeneous green body with sufficient green density is also required.

Another interesting feature of nanoprocessing is to obtain a homogeneous distribution of additives on sub-μm or μm-size powders. As is generally known, it is extremely difficult or nearly impossible to produce weakly agglomerated particles below 1 μm by mechanical milling, and sintering additives used in low concentrations cannot be homogeneously distributed. If nanoparticles can be attached to the surface of larger particles, the additives can be fixed at the place where they are needed, namely on the particle surface.

A third option for the application of nanoparticulate systems is the field of ceramic micro-systems with the aim of keeping the defect size on the lowest possible level.

As can be easily understood, the control of the particle-to-particle interaction plays the most important role for obtaining sufficient green density as well as for the homogeneity, and is also important for the viscosity of slips. For the control of the particle-to-particle interaction, the concept of "surface lubrication" by adsorption of oligomers or polymers on top

of the particle surface was used for conventional ceramic wet processing. The adhesion of oligomers or polymers on solid surfaces is obtained by a multiple adsorption process in which one and the same macromolecule is able to develop numerous adsorption sites. This leads to a good adsorption of the macromolecules on surfaces even if the adsorption versus desorption equilibrium of one single group is poor. The use of oligomers or polymers in nanoparticle processing, however, does not lead to success because the molecular weight of these components is too high compared to the nanoparticles, resulting in a far too high organic concentration in the green body.

In order to overcome these difficulties, the so-called short organic chain molecule surface modification concept was developed. In this case, strong bonds to the surface have to be present because the concept of multiple adsorption cannot be used due to the existence of only one or two adsorptive sites per molecule. A variety of investigations have been carried out in order to seek appropriate bonding mechanisms to the surface [20, 21]. It was shown that the chemistry of surface ions in nanoparticles does not differ markedly from solution chemistry of ions. If one compares the infrared spectrum of a zirconium alkoxide reacted with a carboxylic acid with a zirconium nanoparticle or a μm particle surface-modified with a carboxylic acid, the frequency shift of the carbonyl grouping

is identical and resembles the frequency of a carboxylate group (**Figures 15 a and b**).

The identical $=C=O$ frequency shift leads to the conclusion that the surface chemistry of nano and submicron particle is very similar, but with μm-size particles, due to the small specific surface area, this is of minor importance. As shown in [22], $Zr(OR)_4$ complexed with methacrylic acid (ma) shows exactly the same $=C=O$ frequency shift as ZrO_2 nanoparticles loaded with ma. Due to the high surface area of the nanometer particle, the potential of these reactions becomes important and provides an interesting tool for a variety of modifications.

Other investigations, for example, with ß-diketones acting as complex formers for ions such as alumina 3^+ or titania 4^+ or zirconia 4^+ can also be used as surface modifiers for nano-particles, and in this case, the same effect can be found, i.e. the shift of the carbonyl frequency to the complexed forms with no difference between the ions in solution and ions on the surface of nanoparticles [22, 23, 24]. Of course, there is a large variety of molecules, for example, short organic molecules with a potential to form strong bonds to the surface. Besides the carboxylic acids and the ß-diketones, proteins can be used as well as chelating agents or (if weak complex formers are needed) ether alcoholates [25]. The main purpose of having strong bonds to the surface is to keep the surface modifier on top of the particles and not in the solution in order to avoid disturbing effects from the modifiers.

Another type of surface modifier is constituted by reactive silanes which can be fixed reversibly on a variety of oxidic surfaces as long as stable metal-oxygen-silicon bonds are formed. If that is not the
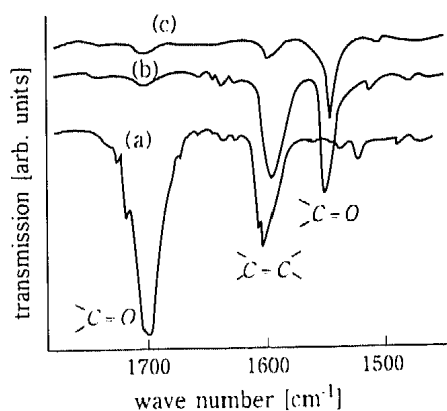
case, these silanes can be polymerized around the particle by first adsorbing them on the surface and then polycondensing them to a silicate "shell" with functional groupings. This type of surface modification was demonstrated on superparamagnetic iron oxide particles [26]. The model is shown in **Figure 16**. The powder obtained is shown in **Figure 17**.

The described principles can now be used for a variety of different purposes. First, if bifunctional groupings with ionic functions are used, the ζ-potential of these particles can be tailored. Tailoring of the surface charge of the nanoparticles opposite to the surface of a large particle leads to a precipitation of the small particles on top of the large particles. This principle can be used for the immobilization of additives. In equation 3, the reaction mechanism for attaching (4 nm) carbon black particles on sub-μm SiC is shown. Carbon black acts as a reducing agent for the removal of the SiO_2 layer [27].
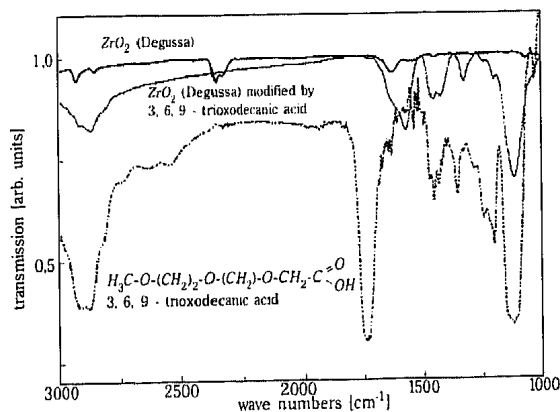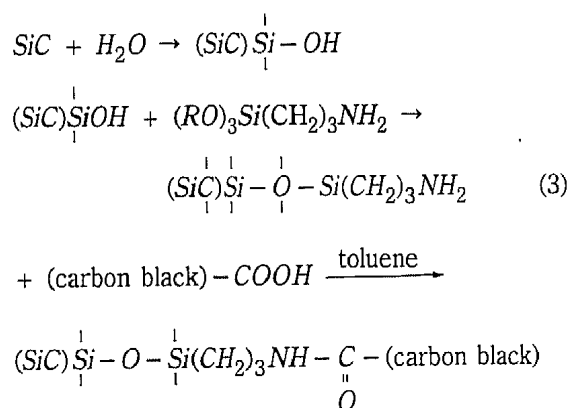
$$SiC + H_2O \rightarrow (SiC)\overset{|}{\underset{|}{Si}} - OH$$

$$(SiC)\overset{|}{\underset{|}{Si}}OH + (RO)_3Si(CH_2)_3NH_2 \rightarrow$$

$$(SiC)\overset{|\ |}{\underset{|\ |}{Si}} - \overset{|}{\underset{}{O}} - Si(CH_2)_3NH_2 \qquad (3)$$

$$+ \; (\text{carbon black}) - COOH \xrightarrow{\text{toluene}}$$

$$(SiC)\overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}}(CH_2)_3NH - \underset{\underset{O}{\|}}{C} - (\text{carbon black})$$

Fig. 15 a-b IR comparison of various ZrO_2 powders loaded with carboxylic acids.

Fig. 15a IR spectra of (a) methacrylic acid (ma); b: $Zr(OR)_3$/ma; c: after hydrolysis, condensation and polymerization of the ma double bond and two weeks water exposure.

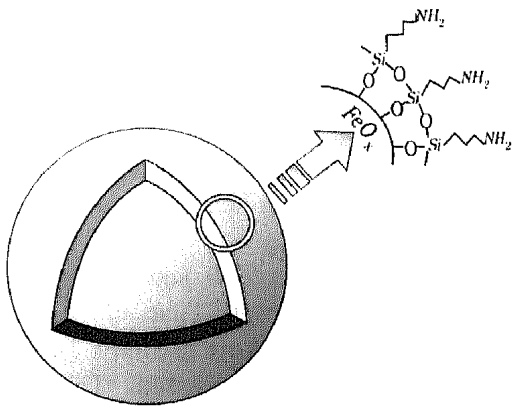**Fig. 15b** ZrO_2 submicron powder of Degussa loaded with aliphatic carboxylic acid.

99

Fig. 16 Model for the surface modification of superparamagnetic iron oxide particles by the formation of a silicate shell [after 26].
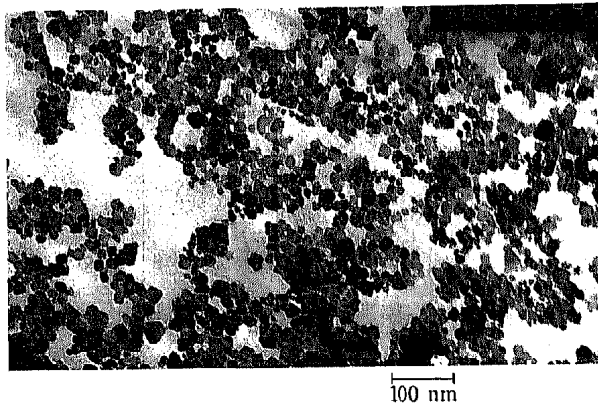

100 nm

Fig. 17 TEM micrograph of agglomerate-free nanomagnetite powder.

The effect of the silane modification on the ζ-potential of SiC is shown in **Figure 18**. It clearly shows the effect of acid and base grouping containing silanes.

High-pressure slip casting processes were carried out and the carbon black distribution was determined [28] (**Figure 19**) over a wall thickness of 12 mm. No concentration gradient was detected.

Silicon carbide powder UF 15 (500 nm) from ESK Company was used for the experiments. The parts were sintered pressurelessly at 2050°C to full density. The microstructure is shown in **Figure 20**.

In **Figure 21**, the difference between the new processing and conventional ball milling in sub-μm high-pressure slip casting is shown. The parts with non-attached carbon black form cracks during firing due to stresses caused by inhomogeneous additive distribution.

Large parts (gas burner tubings of 0.1×0.8 m) as well as gas ignitors showing high thermoshock resistance were fabricated.

These results show that by using nano technologies in wet powder processing, substantial advantages
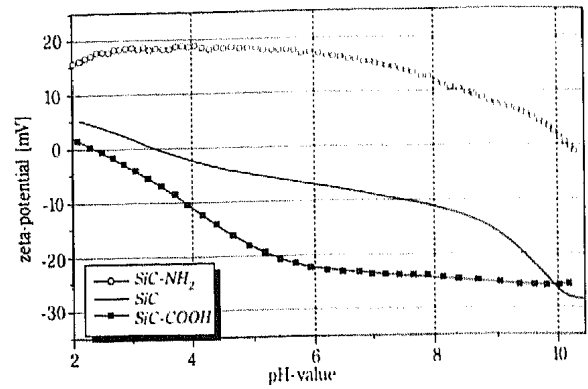

Fig. 18 Effect of surface modification on the ζ-potential of SiC.
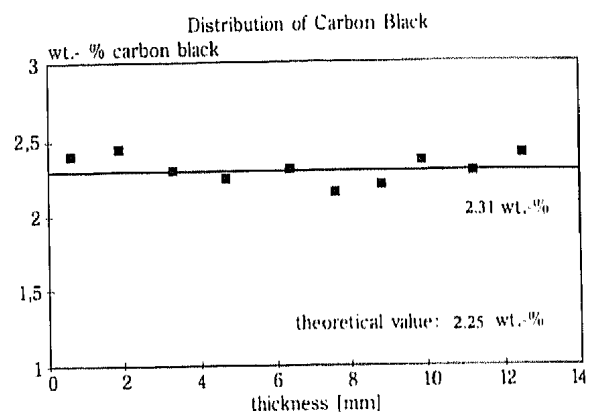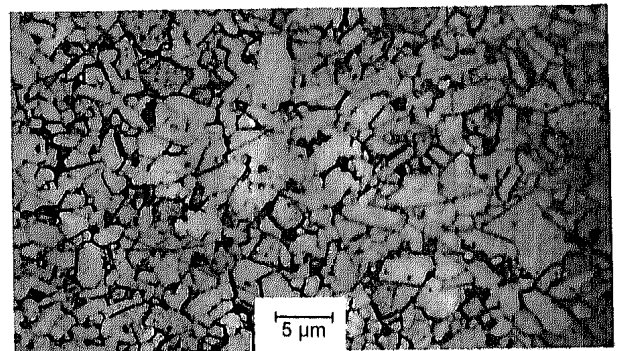

Fig. 19 Distribution of carbon black in ceramic parts in walls of 12 mm thickness.

SEM micrograph of pressureless sintered SiC using carbon black-modified SiC powder and B_4C as sintered aid

Fig. 20 Microstructure of pressureless sintered high-pressure slip-cast SiC (density: 99.7% of theoretical density; strength 700 MPa; K_{Ic} 2.5 MN/m$^{3/2}$).

compared to conventional techniques can be achieved.

Another example for nano processing was carried out with titanium nitride [29]. Titanium nitride is fabricated by the so-called CVR process (chemical vapor reaction) by reacting titanium chloride with ammonia (H.C. Starck company). The titanium nitride powders as produced are heavily agglomerated with agglomerate sizes up to several hundred nm. In
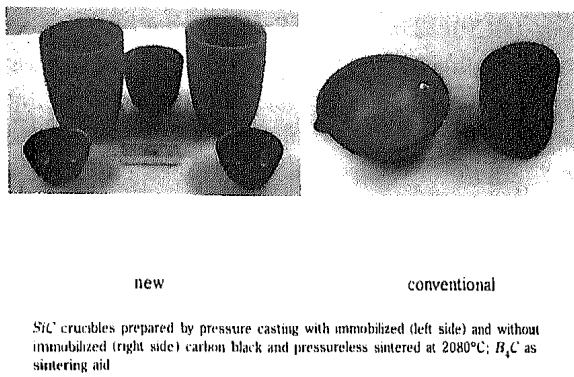
100

new   conventional

SiC crucibles prepared by pressure casting with immobilized (left side) and without immobilized (right side) carbon black and pressureless sintered at 2080°C; B_4C as sintering aid

Fig. 21 SiC parts fabricated by two slip casting methods.

Figure 22, the effect of dispersing agents is shown as determined by photon correlation spectroscopy.

In order to develop a nano processing technique, a deagglomeration technique was developed. Several dispersion agents were tested.

It clearly shows that guanidino carbonate is the most effective dispersing agent. This is attributed to a complex formation to the titanium 4^+ which covers the surface of the titanium nitrite in a thickness of about 1 nm, as determined by ESCA profiling. The effect on the ζ-potential is shown in **Figure 23**.

The guanidino-carbonate-modified titanium nitride can be processed by combined slip casting and colloidal pressing to ceramic green parts with 60% by volume of titanium nitride and sintered to compact parts at temperatures around 1250°C without using pressure [29]. The hardness of these systems is considerably higher than that of conventionally processed titanium nitride which has to be sintered under pressure at temperatures of more than 2000°C.

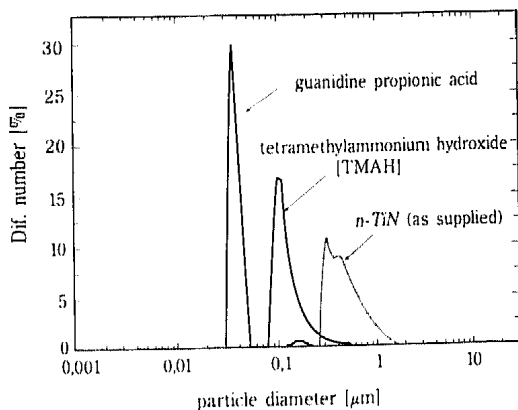In **Figure 24**, the effect of the grain size of the sintered parts on the Vickers hardness is shown.

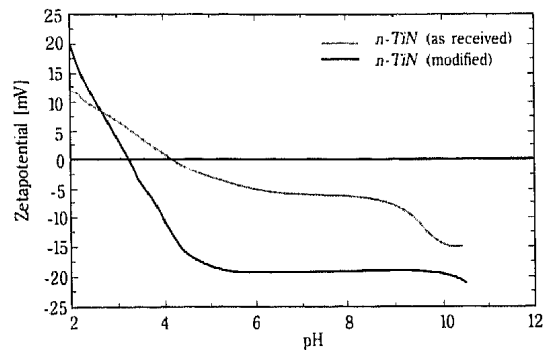**Fig. 22** Effect of different dispersing agents on the disposition of n-TiN powder.

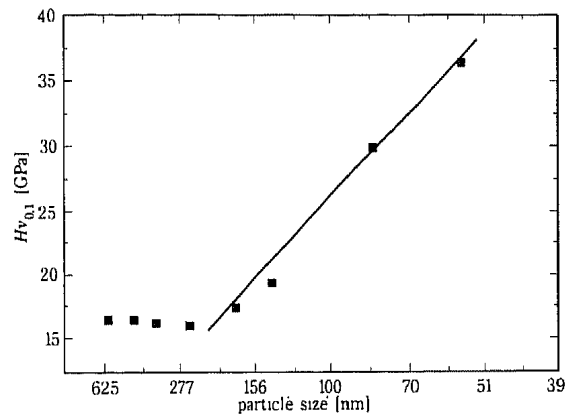**Fig. 23** ζ-potential of n-TiN as received and guanidino-carbonate-modified.

Fig. 24 Hardness of nanocrystalline titanium nitride as a function of grain size.

In **Figure 25**, the sintering behaviour is shown and compared with μm-sized particles.

One can clearly see that the sintering temperature is substantially lower than that of μm TiN, but it can also be seen that the grain growth during the densification step up to 1250°C is almost negligible. Above this temperature, rapid grain growth takes place. These systems can be deformed at pressures of 20 MPa at 1150°C.

Similar results have been obtained from n-zirconia. The X-ray patterns and the sintering behavior of $nZrO_2$ (obtained by the CGP process) are shown in **Figure 26 a-b**. The X-ray pattern in **Figure 26a** clearly depicts the nanoparticle size by line broadening.

It clearly shows the decrease of sintering temperatures as a function of the particle size.
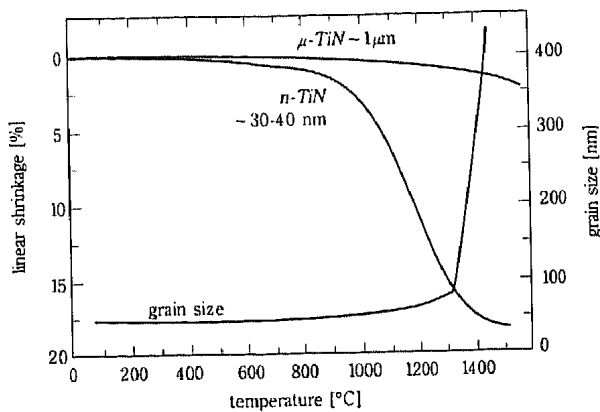
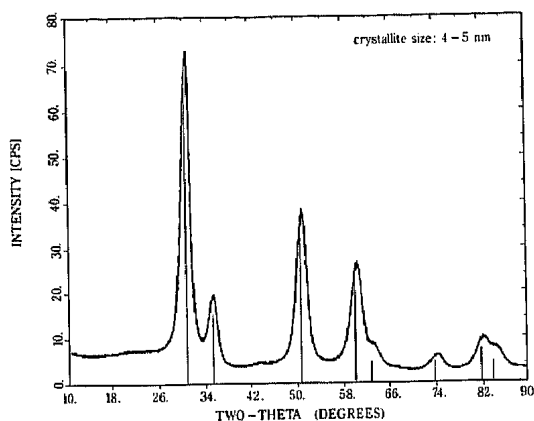**Fig. 25** Sintering behavior and grain growth of *n-TiN*.

Fig. 26a X-ray patterns of *n* ZrO_2 obtained by the CGP process, and sintering behavior compared to μm ZrO_2 (5Y-ZrO_2, tetragonal full lines).
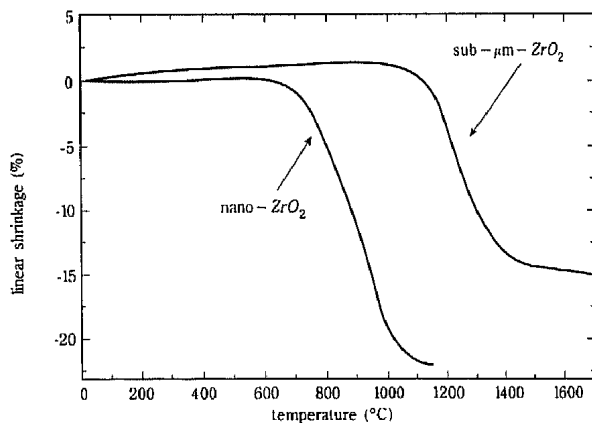

Fig. 26b X-ray patterns of 45 nm ZrO_2 agglomerate size obtained by the CGP process, and sintering behavior compared to sub-μm ZrO_2 (5Y-ZrO_2, tetragonal).

5. Conclusions

A new approach was realized for the chemical synthesis and the processing of ultrafine ceramic powders based on the concept of the control of the surface free energy either in a liquid-liquid system

(MEP) before and after precipitation or in a liquid-solid system (GCP). The crystallization can be carried out by using solid-liquid reaction principles at higher temperatures and higher pressures in closed systems as developed for ZrO_2. Under these conditions, a crystallization (or recrystallization) process takes place, and fully densified crystalline particles can be obtained (e.g. tetragonal phase in the system 5Y-ZrO_2). In order to prevent aggregation, surface modification has to be obtained during this process. If surfactants with a medium chain length are used, they have to be exchanged for short organic molecule surface modification agents in order to reduce the overall organic content of the system. For this purpose, a variety of components can be selected showing good surface interaction with the particle. Examples are ß-diketones, amines, ether ethonalates, complex formers, chelating ligands or proteins. With these systems, it is possible to process the particles by tailoring their ζ-potential for modifying larger particle surfaces for the preparation of stable slips or for obtaining high package densities in green bodies composed of nano particles. Another option of these ceramic particles is to use them in particle technologies such as nanoparticle-containing fluids (magneto or electrorheologic) or pharmaceutical applications, or to use them with appropriate surface modification to incorporate them into organic polymer systems to ultimately produce a new type of inorganic-organic nanoparticle-containing composite (Nanomers).

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