SOL-GEL PROCESSING OF CERAMICS

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ABSTRACT

The sol-gel process can be considered as an interesting method for the synthesis of tailor-made ceramic raw materials. Two points of view are of special interest: powder synthesis and the processing of ultrafine raw materials. In the case of powder synthesis, high quality and multicomponent powders can be synthesized by control of surface chemistry and agglomerate-free subμm powders can be obtained. The preparation of tailor-made sols offers the possibility of powder-free processing of coatings, fibers and microstructure controlled ceramics with small defect sizes. In this paper basic principles and examples for synthesis of powders and processing of ultrafine powders or suspensions will be presented.

INTRODUCTION AND GENERAL CONSIDERATIONS

Ceramic materials are gaining importance in various technological fields, like structural applications, and in functional applications which are especially interesting if combined with micro techniques. In each of these fields, defects in ceramic parts play the most important role with respect to structural as well as to functional properties [1,2]. The ideal ceramic process would be based on extremely well characterized ceramic powders of tailored particle size, size distribution and surface chemistry, high purity and, in case of

multicomponent or additive containing systems, of high homogeneity. A contamination-free processing technology would be available leading to defect-free green bodies with unimodal pore size distribution in the nm range, and the sinter activity of the particles would be high enough to enable low temperature sintering without subsequent crystallization. The desired microstructure tailoring then could be obtained by heat treatment. It is pretty clear, that this is still in the future but one has to think about how to get closer to these goals.

The raw materials used in advanced powder processing techniques presently range from about 0.1 to 10 μm where the lower numbers are still more or less in the experimental stage. There are few sufficient commercial sources of these ultrafine powders and there are extreme difficulties when processing these ultrafine powders. The synthesis and processing of nanosized materials has become an interesting subject in research but there are neither reproducible technologies for large scale powder production nor do processing techniques exist to use these powders or slips in conventional processing or molding techniques. The main preparation techniques are vacuum or plasma techniques or precipitation techniques from homogeneous phases where most of them are only on a preindustrial level. A consequence of this situation is a lack of processing techniques to exploit the potential of the finely divided raw materials.

The chemical route to ultra or nano range ceramic raw materials has important industrial potential, if some of the severe problems can be solved like high volume yield, possibility of preparing multicomponent materials with dopants or additives, or the avoidance of hard agglomerates even in the nano range. This consideration inevitably leads to the necessity of regarding the following steps of processing (powder or powder-free), and one important problem we have to overcome is the surface tailoring to obtain high solid contents. For example, if the slip stabilisation is carried out in an aqueous media, surface charge has to be controlled in order to avoid aggregation (ξ potential control). The resulting electric double layer leads to a remarkable

decay of the solids content with decreasing particle size (under the assumption of the electric double layer being independent of particle size [3]). As shown in Fig. 1, the "electric" approach (by HNO_3) leads to a maximum solids content of 12.5 vol.-%, at 50 nm particle radius, assuming a double layer thickness of 50 nm. The steric approach which was carried out with 50 nm boehmite coated with short chain aliphatic compounds for comparison [4] leads to an remarkable increase of the packing density. The density can be increased up to viscosities suitable for extrusion. In this case, a powder-free processing seems to be achievable.
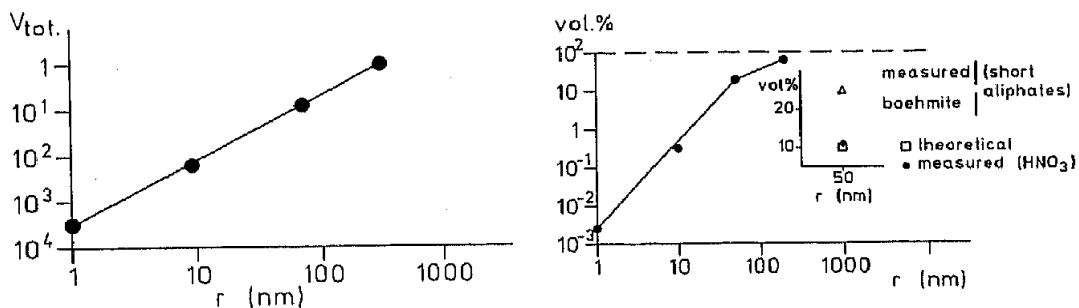

Fig. 1a/b. Dependence of packing density on particle size; comparison of electric double layer with coating; assumed double layer thickness 50 nm; viscosities ≈ 100 mPa·s. $V_{tot.}$ represents the volume fraction of the ceramic particles; r = particle radius; □ = theoretical with 50 nm double layer.

The tailoring of the particle surface, which is a surface chemistry or colloidal chemistry problem, is not systematically investigated with respect to small ceramic particles. The interaction with micelle forming additives is an important possibility to obtain high packing densities and to control interactions between particles, as indicated by [5-7]. In this paper, the scope of the sol-gel process will not

be considered as a method only to synthesize ceramic materials but will be understood as a method for controlling surface chemistry, too, and thus being an important tool to tailor processing properties.

THE SOL-GEL PROCESS

Chemistry and Growth Reactions

The sol-gel process is understood as a method to synthesize ceramic particles or polymer type structures from solution. It can be distinguished from precipitation by its specific property to stabilize a finely dispersed (mostly colloidal) phase in solution by surface chemistry. Very often, the potential of the surface chemistry control is not exploited enough and thus, gelation takes place by formation of an "infinite agglomerate". As a function of concentration, the agglomeration can be kept extremely small as shown by Matijévic [8]. According to La Mer's model, the solubility or the saturation concentration plays an important role. Strehlow [9] was able to calculate stability for monodispersed systems as a function of surface tension and solubility. In [7] the influence of parameters strongly affecting the thermodynamics of the system are shown with ZrO_2 as an example. The "monosized" region of ZrO_2 colloids was determined experimentally and the result is shown in Fig. 2a. In Fig. 2b the effect of the change of one parameter, the complex former concentration, governs the particle size, if one remains within the monosized region. Analysis of the solution phase of the equilibrium state shows a surprisingly high ZrO_2 content (≥ 10 wt.-%). This indicates that the stable sol state is a real equilibrium state. SEM analysis shows a sub structure consisting of nanosized primary particles, indicating a Smochulowski growth model [10].

The complex former seems to be responsible for the limitation of the primary particle size, as demonstrated very clearly with $Al(OR)_3$. The primary particle sizes in sols can be established in the range between 1.5 up to 30 nm only with varying the complex former [11]. These sols show opportunities to be used in a variety of processes. They can be used

ZrO2 mono dispersed powders
Zr concentration: 0 3
1,5 mole menthanol

mole HNO3
mole Zr

mole H2O
mole Zr

—acacH—
mole acacH/mole ZrO2

diameter (μm)

1,2
1,0
0,8
0,6
0,4
0,2

0,1   0,3   0,5 0,7 0,9
   0,2   0,4   0,6 0,8 1,0
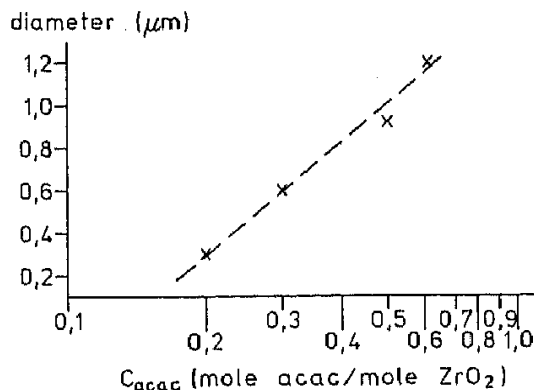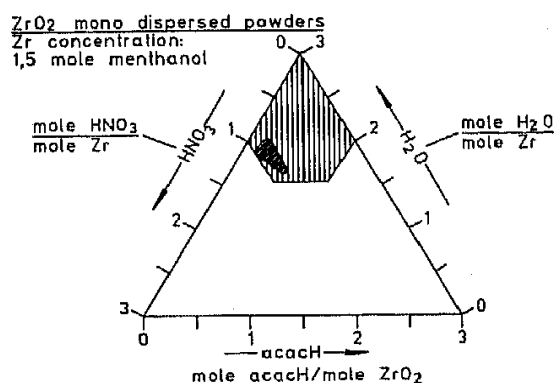
C_{acac} (mole acac/mole ZrO2)

Fig. 2a/b. Monosized particle formation from $Zr(OR)_4$ alkoxides. a: Domain in the three-component system; hatched area: experimentally investigated, formation of polydispersed powders; small area: composition of the formation of monosized powders. b: Dependence of par-ticle diameter on complex former ratio (acetylacetone).

advantageously for coating techniques (crack-free coatings up to 1 μm thickness can be obtained easily by one step dip coating) or for fiber drawing. The solid content of these gels is comparatively low (10 - 15 wt.-%).

The growth controlled formation of oxide particles from solution suffers from several factors concerning thermodynamics: The growth reaction is extremely sensitive to reaction parameters like concentration and composition, and therefore, large scale production becomes very difficult. The control of the process of multicomponent systems requires a very detailed knowledge of the interaction of the different components. The problems connected to such systems with a few exceptions are very difficult to be solved [12].

Another route to obtain spherical particles is the preparation of emulsions [13-15]. In this case, a sol-gel reaction is carried out in "mini" reactors of a dispersed liquid phase in another one. The stability of these emulsions is determined by the

interfacial tension of the two systems, which has to be controlled by surface active additives (Fig. 3). The maximum stability of an emulsion is obtained if $\sigma_{I/(I/II)}$ and $\sigma_{II/(I/II)}$ both become 0 (σ = interface tension) that means the surface active molecules should have two ends, showing chemical properties matching with the two phases. In the case of a water in oil emulsion the oil or hydrocarbon phase can be chosen very easily, but it is much more difficult to adapt the hydrophilic end to the requirements of a variety of aqueous precursors. As shown in [6], Y-doped ZrO_2 could be prepared down to 100 nm diameter. Meanwhile, the droplet size of the emulsion could be reduced to less than 50 nm [16] and nanosized powders down to 20 nm in diameter are expected from these emulsions. To form precipitates in these solutions, precipitation conditions have to be established, for example, by temperature, pH, or specific chemical reaction (e.g. UV induced polymerization, poly-condensation [17]. In [6], the pH change was performed by ion exchange and the transport molecule for ions (phase transfer catalyst, PTC) was found out later to be responsible for an additional micelle like coating of the solidified particle, thus being able to avoid agglomeration completely (Fig. 4.).
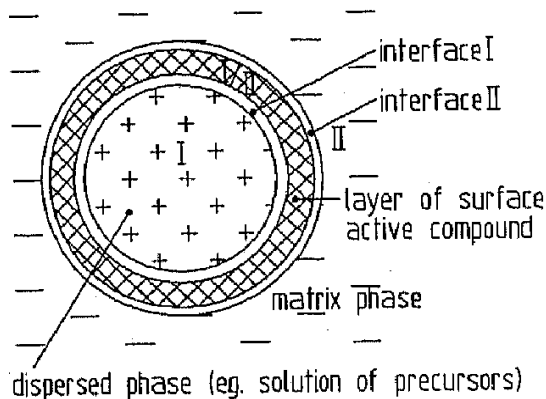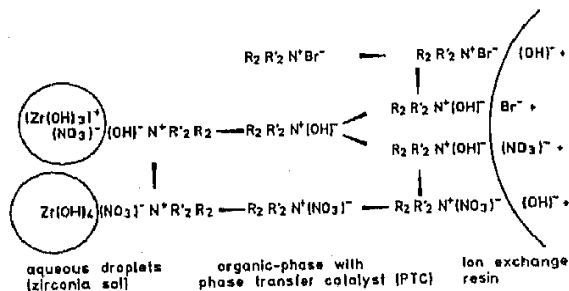

Fig. 3. Schematics of emulsions.

Fig. 4. Effect of PTC for the micro emulsion ion exchange based sol gel reaction.

These powders can be processed directly into ceramics by various processing techniques. In the case of mullite, it could be shown that a bimodal particle size suspension can be obtained, leading to a remarkable improved densification behavior (> 96 % theoretical density at 1300 °C) compared to 86 % in the monomodal case. Summarizing one can say, that chemical surface control will be an important future way for ultra and nanosized sol-gel derived ceramic raw material synthesis and processing.

Processing

The complexed amorphous alumina gels show interesting crystallization properties. The acac-complexed sols seeded with α-Al$_2$O$_3$ show the almost fully developed α-phase at 850 °C with no other phase in between [18]. The analysis of the densification kinetics lead to the conclusion, the activation energy of densification can be influenced by seeding and type of complex former (Fig. 5a/b).
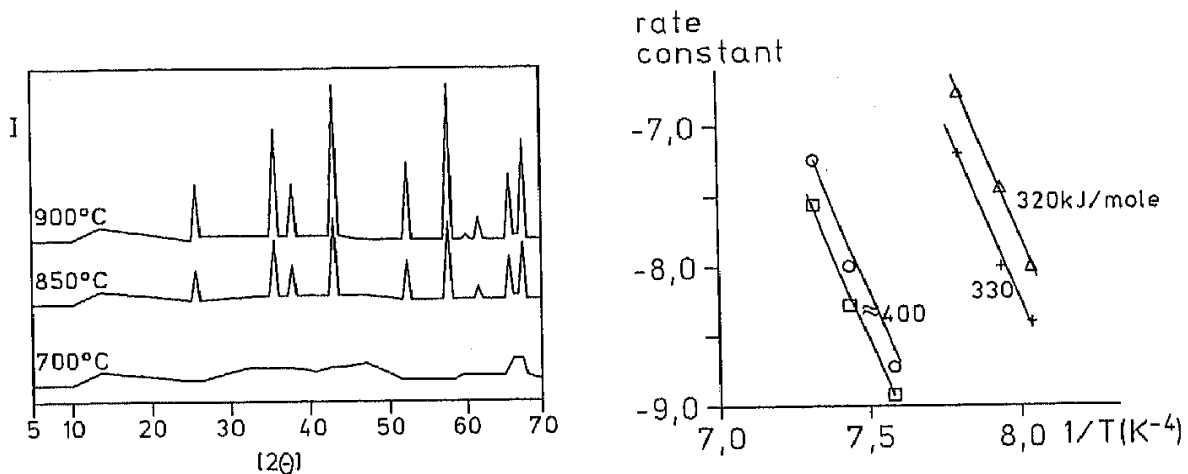

Fig. 5a/b. α-phase development and activation energy for densification in complexed alumina gels. ($\square$) ethylacetoacetate (EA), (o) acetylacetone (acac) without, (+) EA and ($\triangle$) acac with seeding.

In contrast to the complexed sols, electric double layer (HNO_3) stabilized Al_2O_3 sols could be "stuffed" up to more than 50 wt.-% Al_2O_3 still showing viscosities allowing infiltration [19]. Based on this, fiber reinforced materials have been developed [20], and a further development by MAN company led to a laminated insulation system for the European space shuttle [21].

If the particle size becomes essentially smaller than 100 nm, conventional molding procedures become extremely difficult. Therefore, the electrophoretic deposition was investigated [22]. The key issue is to avoid electrolysis and from this, the use of organic solvents is preferable. Sufficient charge has to be fixed to the small particles which can be done by polymeric ionic compounds, for example polyacrylic acid. It is of extreme importance to tailor the system by proper surface chemistry (binding the charge carrier completely to the surface). If this can be carried out properly (e.g. by control of the adsorption isotherms), surprising effects can be obtained, e.g. in the case of Al_2O_3 (commercially available powders, 0.1 μm fraction) the deposition rate can be increased up to $\approx$ 1 $g \cdot cm^{-2} \cdot min^{-1}$ with deposition voltages up to 1200 V (Fig. 6). The benefits of this process are ceramic components
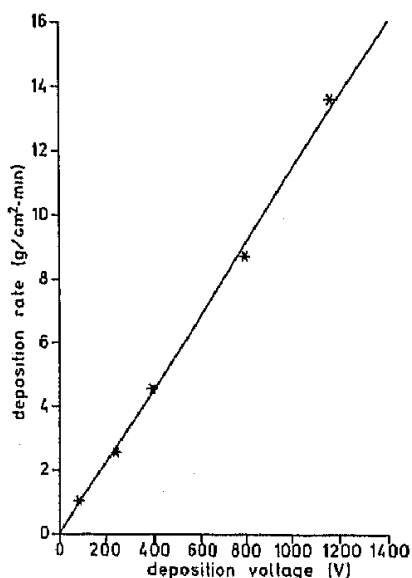

Fig. 6. Deposition rate as a function of deposition voltage.

through green bodies with narrow monomodal pore distribution, exhibiting very high strength compared to other molding techniques [22]. Several other systems have been investigated, like SiC or SiO_2 or nanosized amorphous alumina (complex stabilized Al_2O_3, ≈ 2 nm particle size [23]. It was proved that sols down to 2 nm can be shaped to ceramic bodies, but drying has to be optimized (Al_2O_3: 2 nm, SiO_2: 5 and 50 nm sols were used). The shaping of 50 nm SiO_2 sols has been successfully carried out by Clasen [24] who was able to produce tubes by this method.

CONCLUSION

Sol-gel processing and related techniques are an interesting method to synthesize and to process ultrafine and nanosized powders but also to avoid the "dry powder" step. Together with closed system preparation techniques and molding techniques tailored for fine particle molding. The process has an interesting potential for a variety of applications (structural ceramics, micro techniques). The control of surface chemistry is one of the key issues and systematic investigations are necessary.

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