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Superfine Oxide Powders—Flame Hydrolysis and Hydrothermal Synthesis

Nanocrystalline Ceramics
Powder Processing
Clean Room Technology
Sintering

By Gangolf W. Kriechbaum * and Peter Kleinschmit *

1. Introduction

The excitement surrounding the technical potential of ceramic materials has gained new support since the surprising physical properties of so-called nanocrystalline materials have been observed.[1] *Gleiter* and coworkers were able to show that a thin ceramic plate of TiO_2 with a nanocrystalline microstructure could be plastically deformed at a temperature as low as 180 °C. This behavior opens the way to new ceramic processing and forming techniques.

In the last decade a lot of research activities have been focused on the development of new synthetic methods for the production of sinter-active submicron ceramic powders. The state of the art of powder synthesis has been reviewed by several authors.[2–6]

This paper describes flame hydrolysis and hydrothermal synthesis, two techniques with the potential to yield superfine powders with a particle size in the nanometer range, and discusses problems involved with the synthesis and handling of superfine materials.

The step from conventional ceramics to high performance ceramics can be described as a change in size range. Conventional technical ceramics with grain sizes between 5 to more than 100 microns and flaw sizes in a similar range are made out of powders prepared by classical mixing-calcining-milling methods or out of refined minerals. High performance ceramics with grain sizes between 0.2 to less than 1 micron need chemically prepared powders in a submicron size range and processing techniques which prevent flaw sizes much bigger than the grain size. By far the most ceramic powders are still produced by conventional techniques but high performance ceramic applications are gaining in importance and therefore the share of chemically prepared powders increases.

Reducing the particle size and increasing the chemical and morphological homogeneity of the powders has led to some specific problems in synthesis and processing.

The need to work in clean rooms or in closed production lines in order to avoid contamination by dust and other particles which are omnipresent in normal unfiltered air is just one example of the required changes for submicron processing.

By improving powder quality and processing techniques and by the design of new microstructures, e.g. the development of toughening concepts like transformation toughening in ZrO_2, a tremendous improvement of strength, toughness and reliability has been accomplished in modern ceramic materials. The nanophase ceramics which go a further step in size reduction are a new challenge to both fields, powder synthesis and processing science.

2. Problems Involved in Processing Superfine Powders

Before synthesis of nanosized powders is discussed, a short description of possible problems involved with the synthesis and handling of fine powders will be given.

2.1. Processing Environment

An overview of the sizes of different airborne particulates is given in Figure 1. To obtain optimal strength and reliability data, maximum flaw sizes in ceramics should be in the range of the grain size. Taking into account that normal air contains between 10^7 to 10^8 particles/m^3 in the micron range, it becomes obvious, that a clean environment is one of the key requirements for submicron processing. This is necessary not only during synthesis but also during handling and shaping. For nanophase materials this becomes even more necessary but clean room techniques are very limited in a particle size range smaller than 0.1 micron.

2.2. Agglomerates and Aggregates

The tendency of fine powders to form uncontrolled agglomerates and aggregates has a strong influence on synthesis and processing. Interparticle cohesion increases strongly with decreasing particle size because of the greater significance of short range, weak forces like electrostatic forces and van der Waals forces, with the result that the strength of agglomerates increases with decreasing particle size. In powders with particle sizes below 50 nanometers strong agglom-

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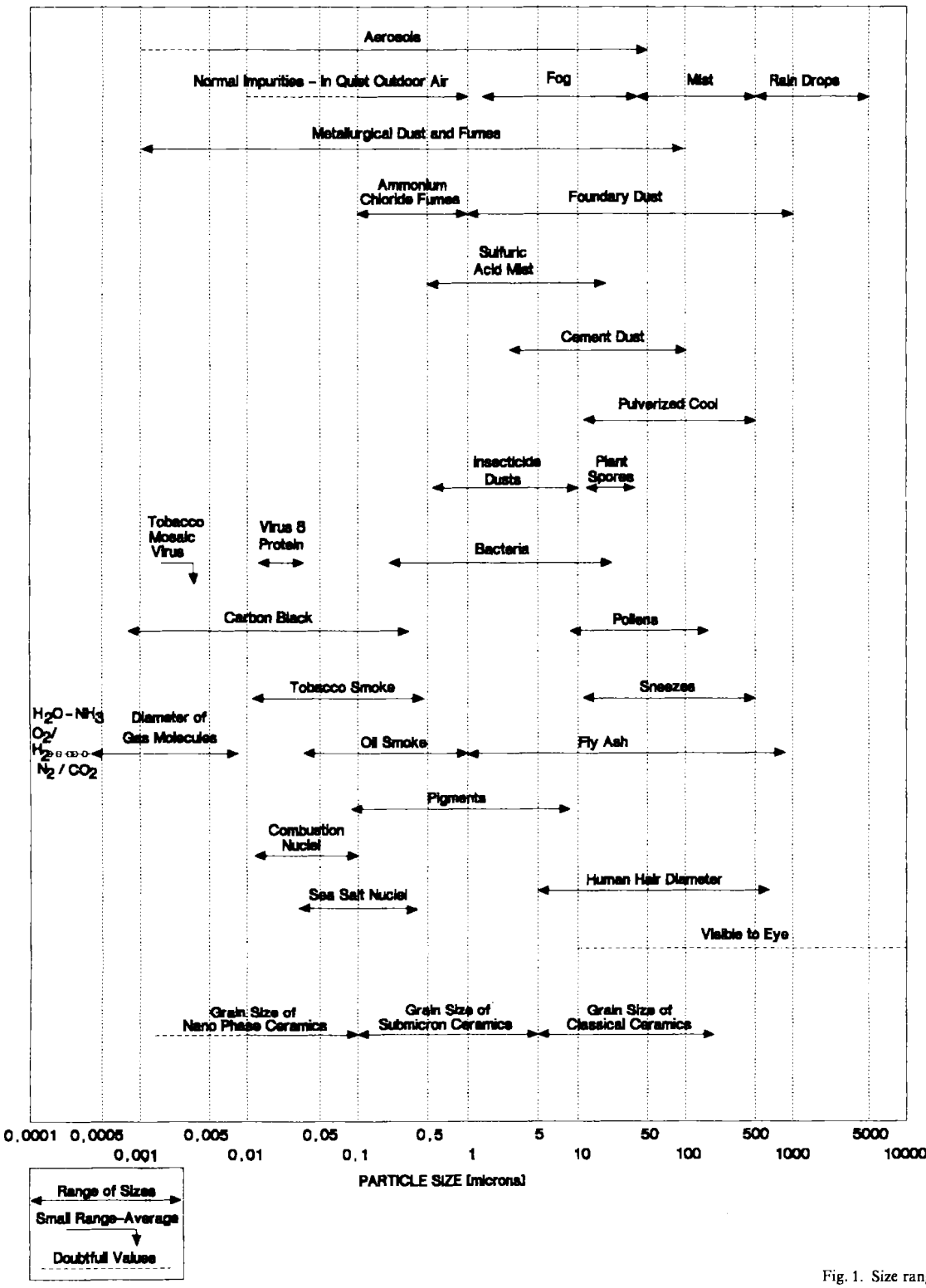


Fig. 1. Size ranges of airborne particulates.

erates can hardly be avoided because of the significance of the van der Waals attraction in this size region.[7] In addition, the increasing specific surface area resulting from the decreasing particle size leads to a greater tendency for vapor condensation on particle contacts. This causes bonds to form between particles and so further strengthens the existing agglomerates.[8] The negative effect of strong agglomerates on powder packing and morphological homogeneity of the green body is well described in the literature.[9-11] Inhomogeneities in the green body lead to structural flaws in the sintered product and increase the necessary sintering temperature because intra-agglomerate sintering occurs at lower

Table 1. Concepts for controlling agglomerates [14].

I	Possible ways to influence agglomerate characteristics during their formation
	1. Optimization of precipitation conditions
	2. Special treatment of precipitates before or during drying
	- Removal of anions
	- Washing with organic liquids
	Freeze-drying
	- Drying in controlled humidity
	- Hydrothermal treatment
	3. Optimization of calcination
II	Possible ways to eliminate or destroy agglomerates after their formation
	1. Sedimentation
	2. Milling
	3. Ultrasonic treatment
	4. Dispersing agents
	5. High forming pressure

temperatures than inter-agglomerate sintering.[12, 13] In addition strength, toughness and reliability are decreased. Several concepts have been developed to improve particle agglomeration in submicron powders.

Recently, techniques for agglomeration control in wet-chemical powder synthesis have been reviewed by *Roosen* and *Hausner*.[14] Table 1 lists the techniques proposed for controlling agglomerate characteristics. To avoid agglomerates during synthesis or to destroy or eliminate agglomerates formed already are the two fundamental possibilities.

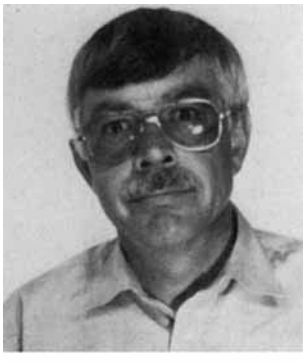
Destroying agglomerates after their formation by milling or sedimentation is limited to powders with agglomerate sizes bigger than 0.1 micron. For nanosized powders, ways to influence agglomerate characteristics during their formation have to be found. This is rather difficult to achieve because the main advantage of superfine particles, their very high sintering activity, becomes a major disadvantage during synthesis. Synthetic methods where high temperatures are involved, promote the formation of aggregates by forming solid bridges on particle contacts.

Therefore low temperature methods like gas-condensation techniques or small particle concentrations during high temperature treatment in a dispersed phase – gas phase or liquid phase – are necessary for the synthesis of weakly agglomerated nanosized powders.

2.3. Forming

The nanocrystalline TiO_2 plate mentioned earlier which showed ductile behavior[1] was shaped by in situ compaction of the powder by dry pressing with a pressure as high as 1.4 GPa.[15] No value of the achieved green density is given nor is it explained why a high pressure far beyond the usual pressure range, was applied. Poor packing of the synthesized powders may be one of the reasons. To obtain homogeneous, dense sintered structures from superfine powders, green bodies with a uniform pore size distribution are required. Since weak forces dominate the packing of dry ultrafine particles, dry forming techniques are not favored.

Wet forming processes like colloidal filtration[16] may be more successfull. Packing of fine powders in suspension can be improved substantially by the use of the appropriate pH range and by organic dispersants. *Sacks* has investigated the packing behavior of fine silica spheres and found that by proper control of the particle dispersion, sintering temperatures can be decreased by increasing the homogeneity of green compacts.[17]



Peter Kleinschmit was born in 1938 in Leipzig (GDR) and studied chemistry at the Universities of Hannover (FRG) and Vienna (Austria) gaining a Ph.D. for a study of "Chemistry in Molten Salts" in 1968. Since then he has occupied various positions with Degussa, starting as a Research Chemist and becoming a Board Assistant in 1970, a Plant Manager in 1973 and the Head of the Inorganic Research Department in 1975.

Gangolf Kriechbaum was born in Nürnberg (FRG) in 1953 and studied chemistry at both the University of Regensburg (FRG) gaining his Diploma in 1981, and the University of Frankfurt (FRG) where he gained a Ph.D. for his work on the "Reactivity of Metal-Metal Multiple Bonds" in the group of Prof. W. Herrmann in 1983. He then spent a year working with Prof. A. Cotton at Texas A & M University (USA) before joining Degussa as a Research Scientist in 1984.

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3. Synthesis of Superfine Powders

The nanophase TiO_2 ceramic described by *Gleiter* and coworkers was made out of a powder which had been synthesized by the so called gas-condensation method.[15] The principle of this synthetic technique is the evaporation of titanium metal in an oxygen free vacuum by resistance heating and the decomposition of the metal vapor on a liquid nitrogen cooled cold finger. Controlled oxidation of the deposited metal powder by introducing oxygen to the reactor finally produces titanium dioxide. The advantage of this method is that it works in a very clean, easily controlled environment.

On the other hand, gas-condensation is limited to very few chemical systems which are not necessarily in the focus of ceramic interest. Also, the turnover limits this technique to small scale operation and therefore other synthetic routes to nanosized powders have to be developed.

Because of their potential to yield superfine powders, flame hydrolysis and hydrothermal synthesis are synthetic routes which are promising for the preparation of suitable powders on an industrial scale.

3.1. Flame Hydrolysis

The reaction of volatizable compounds like for example $TiCl_4$ or $SiCl_4$ in an oxygen-hydrogen flame leads to highly dispersed oxides. This technique, called flame hydrolysis or the AEROSIL process, was originally developed by *Klöpfer*[18] and has been designed to make highly-dispersed silica. Meanwhile, flame hydrolysis has been used to produce a variety of different compounds, some of which are listed in Table 2.[19–21] A flow sheet of the process is shown in Figure 2. Silica, alumina and titania are produced on a commercial scale and have found numerous industrial applications, for example, as fillers and thickeners.[19]

Table 2. List of pyrogenic products [18].

Product	Raw Material	b.p. [°C]
SiO_2 [1]	$SiCl_4$	57
Al_2O_3 [1]	$AlCl_3$	180 [3]
TiO_2 [1]	$TiCl_4$	137
ZrO_2 [2]	$ZrCl_4$	331 [3]
ZrO_2/Al_2O_3 [2]	$ZrCl_2/AlCl_3$	331 [3]/180 [3]
ZrO_2/TiO_2 [2]	$ZrCl_2/TiCl_4$	331 [3]/137
Al_2O_3/TiO_2 [2]	$AlCl_3/TiCl_4$	180 [3]/137
$AlBO_3$ [2]	$AlCl_3/BCl_3$	180 [3]/12
$AlPO_4$ [2]	$AlCl_3/PCl_3$	180 [3]/74
Bi_2O_3 [2]	$BiCl_3$	441
Cr_2O_3 [2]	CrO_2Cl_2	117
Fe_2O_3 [2]	$FeCl_3$	319
	$Fe(CO)_5$	103
GeO_2 [2]	$GeCl_4$	84
NiO [2]	$Ni(CO)_4$	42
MoO_3 [2]	$MoCl_5$	268
SnO_2 [2]	$SnCl_4$	114
V_2O_5 [2]	$VOCl_3$	127
WO_3 [2]	WCl_6	346
	$WOCl_4$	228

[1] commercial. [2] laboratory product. [3] sublimation point.

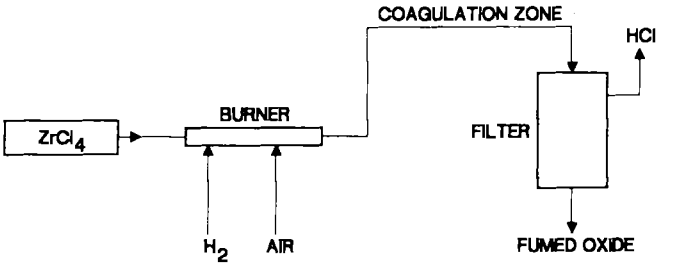

Fig. 2. General flow sheet for the preparation of ZrO_2 by flame hydrolysis [22].

The major advantages of flame hydrolysis are the high purity of the compounds, its chemical flexibility, and the possibility to synthesize mixed oxides which are homogeneous even on a molecular scale. In addition, powder properties like specific surface area and particle size can be easily controlled by varying the reaction conditions. The most important disadvantage for ceramic use is the very low bulk density of pyrogenic materials. Figure 3 shows transmission electron micrographs of some of the commercially available silica powders. Powders with particle sizes between 7 and 50 nanometers and specific surface areas between 50 and 380 M^2/g can be synthesized. For ceramic applications the chemical systems ZrO_2,ZrO_2–Al_2O_3, Al_2O_3–ZrO_2 and Al_2O_3–TiO_2 are of interest.

Promising results have been obtained on zirconia powders, synthesized by flame hydrolysis.[22] Powders with specific surface areas between 20 and 100 m^2/g and a particle size between 10 and 50 nm have been prepared. X-Ray diffraction (XRD) analysis showed that the pyrogenic ZrO_2 crystallizes in the tetragonal phase with only a small monoclinic part. The "as prepared" powder has a very low bulk density of about 150 g/l and therefore precompaction is necessary. The sintering experiments were performed on powders which were yttria doped and precompacted by spray drying. Densities of about 99% of theory were achieved at a sintering temperature of 1450 °C. The relatively high sintering temperature caused grain growth so that grain sizes of about 0.2 micrometers were obtained. The originally nanosized powder only preserves its size range when the applied sintering temperature is much lower.

The same authors have made silica stabilized aluminum titanate powders by cohydrolysis of $SiCl_4$, $AlCl_3$ and $TiCl_4$. The transmission electron micrograph of the powder shows spherical particles in a size range between 20 and 100 nanometers (Fig. 4).

Cold isostatically pressed compacts were densified at a temperature as low as 1300 °C to a density of more than 3.6 g/cm^3 and showed a grain size of much below 1 micron, which is rather small for aluminum titanate (Fig. 5). By flame hydrolysis with a specially designed burner nanosized zirconia powders have been coated with alumina.[23] The synthesized Al_2O_3–ZrO_2 particles have a size between 40 and 100 nm. Data on the sintering behavior of this material have not been published.

Pyrogenic aluminas differ fundamentally in their properties from other aluminas which are prepared by precipitation

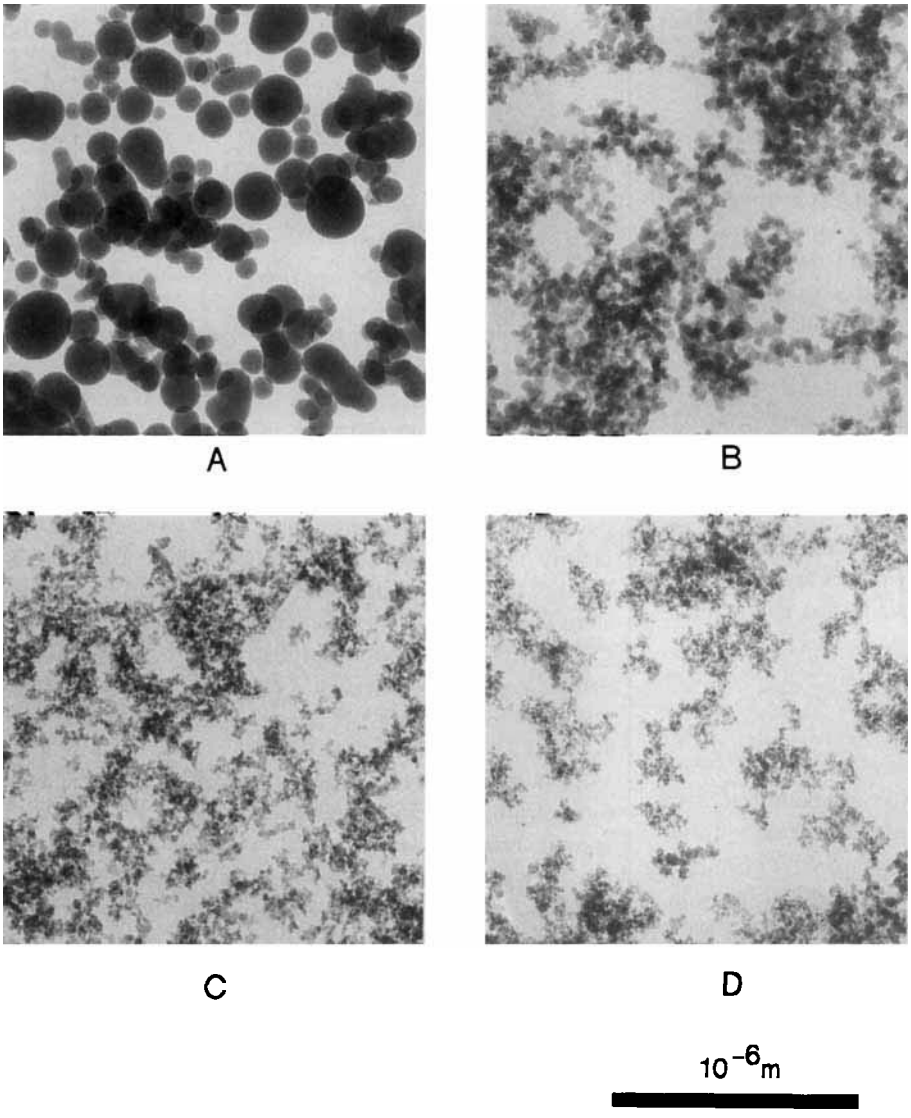

Fig. 3. Transmission electron micrographs of commercial silica powders prepared by flame hydrolysis with different specific surface areas. A: 50 m^2/g, B: 130 m^2/g, C: 300 m^2/g, D: 380 m^2/g. Mag. 1:50000.

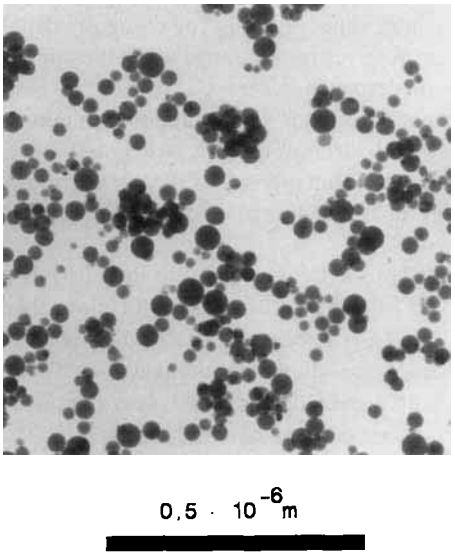

Fig. 4. Transmission electron micrograph of a pyrogenic Al_2O_3–TiO_2 powder (Mag. × 100000).

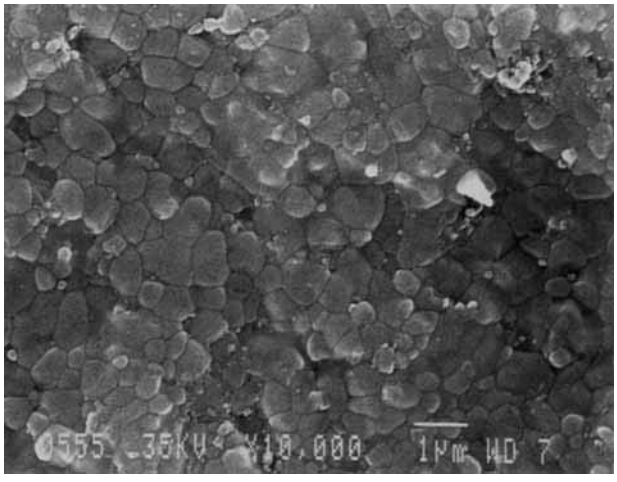

Fig. 5. Scanning electron micrograph of a fracture surface in sintered Al_2TiO_5 prepared from pyrogenic powders (Sintering temp. 1300 °C, 2 h).

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and/or solid state reactions. They have a primarily gamma structure with traces of delta and have a particle size of about 15 to 20 nm with a specific surface area of about 100 m^2/g.[19] Sintering of the "as prepared" powder is not very successful because of the phase transformation to α-alumina during the sintering process. A high sintering activity has been reported by *Kato* et al. when the chemical vapor deposition CVD derived Al_2O_3 powder was precalcinated at 1200 °C to 1350 °C. During the calcination process particle growth occurs and powders with particle sizes between 0.1 to 0.5 are obtained.[24] It has not been reported that nanosized alumina can be synthesized in its α-form by flame hydrolysis.

3.2. Hydrothermal Synthesis

Reactions in water above its boiling point and therefore under pressure, are called hydrothermal reactions. This very general definition illustrates that a variety of very different chemical processes are categorized under the heading hydrothermal reactions.

Historically the first hydrothermal experiments were performed by *Schafhäutl*[38] who synthesized quartz crystals from amorphous silica although nature used hydrothermal reactions long before for the formation of numerous minerals. Although hydrothermal processing is a familiar technique very few examples of commercialization are known. Most important is the Bayer-process which includes a hydrothermal leaching step to form soluable sodium aluminates for separation from remaining solids. The synthetic and hardware aspects of hydrothermal synthesis have been reviewed by *Rabenau*.[26] This paper is limited to hydrothermal processes connected to superfine ceramic raw materials.

The different hydrothermal reaction types described in the literature are decomposition, oxidation, crystallization, precipitation, sintering, and leaching. For the synthesis of superfine ceramic oxides only hydrothermal precipitation and hydrothermal crystallization have to be considered. General flow sheets of both techniques are shown in Figure 6. While hydrothermal precipitation starts from clear metal salt solutions, hydrothermal crystallization uses hydroxide gels or sols. Hydrothermal synthesis yields oxide suspensions of crystalline metal oxides which in some cases can even be used for ceramic processes without a calcination step. A variety of different oxides have been synthesized by hydrothermal techniques (Table 3). For structural ceramics, zirconia, alumina, titania and mixed powders like Al_2O_3–ZrO_2, ZrO_2–Y_2O_3 and Al_2O_3–TiO_2 are the most relevant systems. As already mentioned, the major advantage of hydrothermal

Table 3. Oxides prepared by hydrothermal synthesis [29].

Oxides	Mixed Oxides	Complex Oxides
ZrO_2	ZrO_2–Y_2O_3	$BaFe_{12}O_{19}$
SiO_2	ZrO_2–Y_2O_3–MgO	$BaTiO_3$
Al_2O_3	ZrO_2–MgO	
TiO_2	ZrO_2–Al_2O_3	

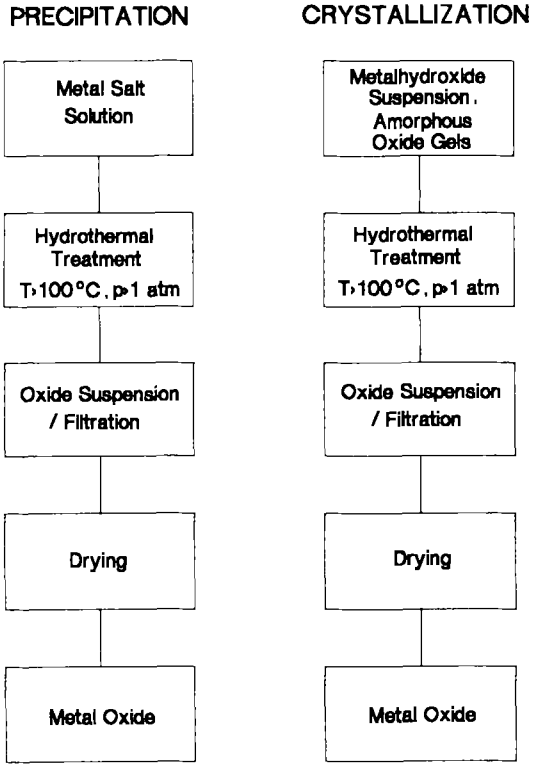

Fig. 6. General flow sheet for hydrothermal precipitation and crystallization.

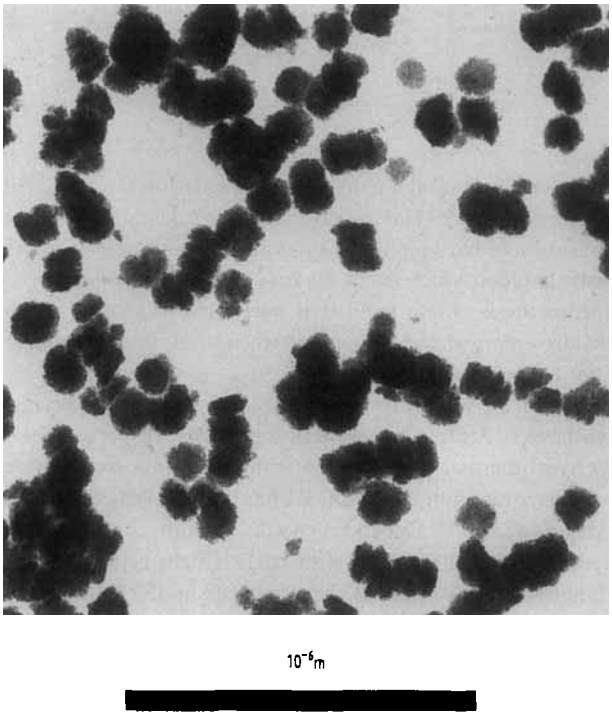

Fig. 7. Transmission electron micrograph of a ZrO_2 powder synthesized by hydrothermal precipitation from a $ZrOCl_2$ solution ($T = 200$ °C). Mag. 1:100 000.

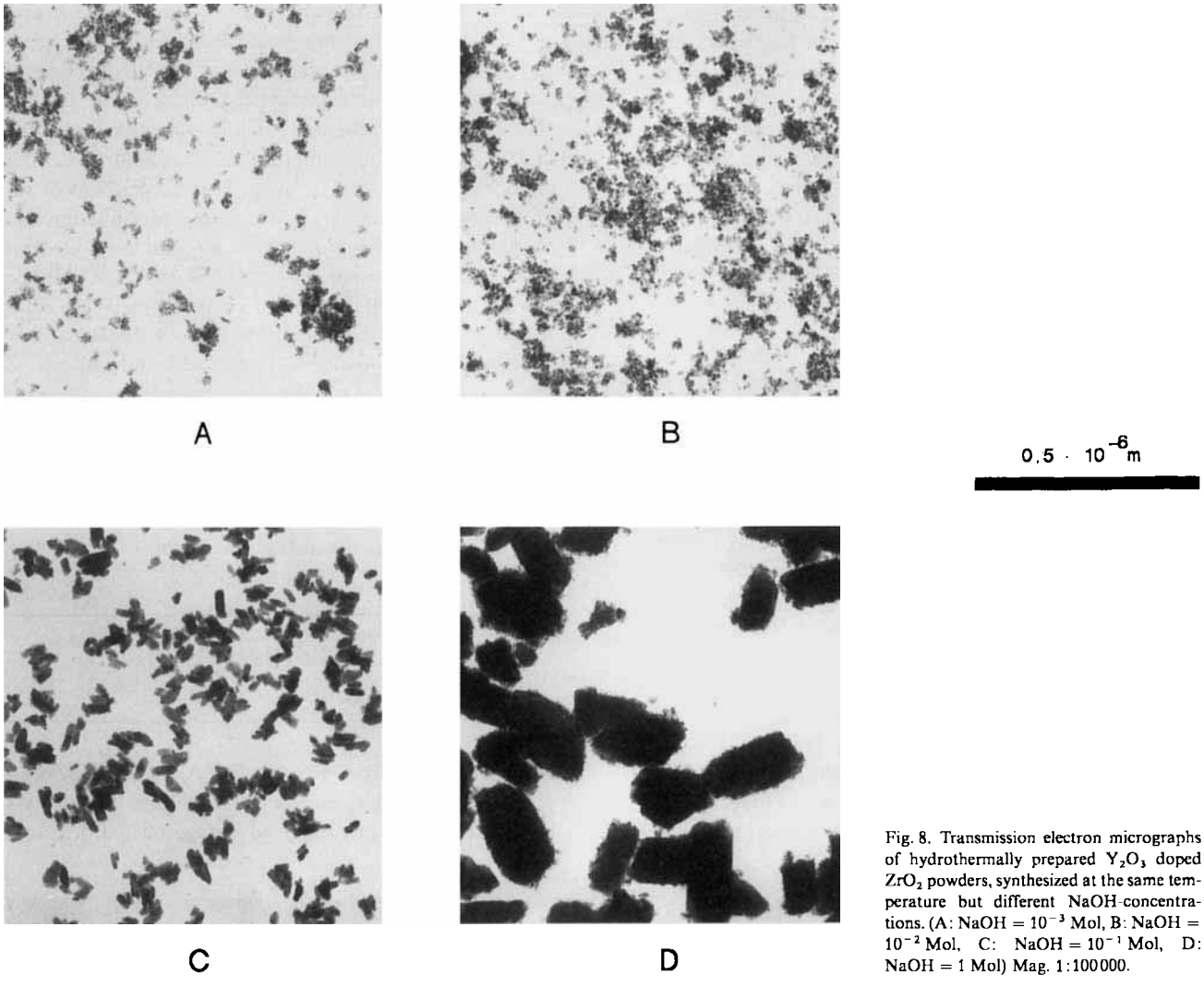

Fig. 8. Transmission electron micrographs of hydrothermally prepared Y_2O_3 doped ZrO_2 powders, synthesized at the same temperature but different NaOH-concentrations. (A: NaOH = 10^{-3} Mol, B: NaOH = 10^{-2} Mol, C: NaOH = 10^{-1} Mol, D: NaOH = 1 Mol) Mag. 1:100000.

processing is that high temperature calcination is not needed to form oxides.[27] Having no solid state calcination step the formation of hard agglomerates and aggregates can be more easily avoided which is not the case in sol-gel or coprecipitation methods where nanosized particles are formed which are also enlarged and aggregated when solid state crystallization to the oxide is performed.

One of the most promising candidates for hydrothermal synthesis is ZrO_2. The formation of highly dispersed ZrO_2 by hydrothermal precipitation from zirconium oxychloride or other zirconium salt solutions has been described by several authors.[27-31] Depending on the reaction conditions anhydrous monoclinic ZrO_2 with particle sizes between 3 and 10 nanometers and surface areas as high as 180 m^2/g can be obtained.

The very fine primary particles are agglomerated into regular shaped clusters in the narrow size range between 0.1 and 0.25 μm (Fig. 7).[32] For use in structural ceramics pure ZrO_2 has to be doped with Y_2O_3. To synthesize homogeneously doped zirconia the described precipitation method has to be modified because Y_2O_3 is not precipitated under acidic conditions.[33]

Using a thermally unstable compound like urea which decomposes at elevated temperatures and so changes the pH to higher values, is one of the possibilities to succeed in synthesizing Y_2O_3–ZrO_2 powders by hydrothermal precipitation.[34] Problems with material corrosion caused by the changing pH values during the reaction may limit this method to small scale production where teflon lined autoclaves can be easily used.

An alternative way to prepare superfine yttria-doped zirconia powders is the hydrothermal crystallization of hydrous zirconium and yttrium oxides.[33] The particle size of the synthesized powders can be varied according to the reaction conditions between 10 to about 500 nanometers.[32,35] Figure 8 shows transmission electron micrographs of yttria-zirconia powders (3 mol-% Y_2O_3) synthesized at different pH values. With increasing $^{\ominus}OH$ concentration, particle size can be increased. Besides size, particle shape can also be controlled by the addition of mineralizers.[36]

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The published sintering results[32, 36] indicate that theoretical densities have almost been obtained with hydrothermal ZrO_2–Y_2O_3 powders. The dilatometer investigation shown in Figure 9, where the sintering behavior of a hydrothermal

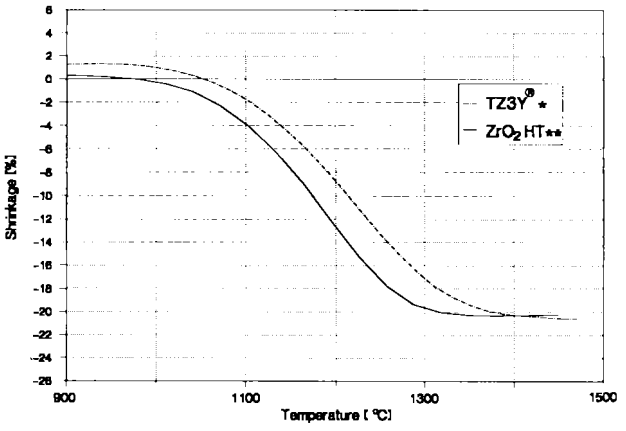

Fig. 9. Shrinkage vs. temperature of two Y_2O_3 doped ZrO_2 powders, one prepared by coprecipitation, (* Tosoh Co.) the other hydrothermally (** Degussa AG)

oxide powder is compared with a powder obtained by coprecipitation, clearly indicates that a decrease of sintering temperature can be achieved.[37] Necessary sintering temperatures are still too high to prevent grain growth during sintering and a grain size of 0.2 micrometer in the dense body is observed.

Hydrothermal crystallization can also be used for the synthesis of CaO,[38] MgO[39] and MgO–Y_2O_3[39] doped zirconia. The synthesis of Al_2O_3 and Al_2O_3–TiO_2 powders by hydrothermal crystallization has also been reported.[36] Published results show however that the powders obtained are not in the nanosized range.

4. Outlook

The synthesis of nanosized powders can be achieved by flame hydrolysis and hydrothermal synthesis. The poor packing of the fine powders is responsible for the fact that the advantages of these super fine materials with respect to sinterability and the possibility of yielding nanocrystalline materials have not been fully exploited. Research is needed to develop appropriate processing techniques for the compaction and the shaping of superfine powders.

Both discussed synthetic routes have already proved that upscaling is possible. If progress in the development of better handling and processing methods is achieved, flame hydrolysis and hydrothermal synthesis will become important techniques for the production of super fine oxidic ceramic raw materials which in turn will further improve the performance of ceramic materials.

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