SYNTHESIS AND COLLOIDAL PROCESSING OF NANOCRYSTALLINE (Y$_2$O$_3$-STABILIZED) ZrO$_2$ POWDERS BY A SURFACE FREE ENERGY CONTROLLED PROCESS

DETLEF BURGARD, RÜDIGER NASS; HELMUT SCHMIDT
Institut für Neue Materialien, Im Stadtwald, Geb. 43, D-66123 Saarbrücken, Germany

ABSTRACT

Using the controlled growth technique, nanocrystalline ZrO$_2$ powders have been prepared from solution. By variation of the Y-content (0-8 mol %), redispersable monoclinic, tetragonal or cubic ZrO$_2$ powders with particle sizes between 5 and 10 nm were obtained after crystallization at elevated temperature and pressure. Nanodisperse suspensions of the powders have been used for colloidal processing techniques such as tape casting, slip casting or extrusion. The resulting green bodies with densities of 55 % and average pore sizes of 5 nm could be sintered at temperatures below 1100 °C leading to monoclinic, tetragonal or cubic ZrO$_2$ ceramics.

INTRODUCTION

The fabrication of advanced nanostructured ceramics requires high quality powders. The prerequirements for these powders are high chemical and crystallographic purity, homogeneity, particle size in the nm-range, redispersability as well as low production costs. A comparision of already described synthesis methode [1-16] shows, that only few of them, especially wet chemical synthesis methods, are able to fullfill all prerequirements. Wet chemical synthesis processes start from molecular or ionic precursors passing a nanosized state. During synthesis the intermediate particulate system tends to minimize its surface free energy by growing larger particles and/or agglomeration. These reactions can be avoided by controlling the the thermodynamics of the interfaces either by restriction of the reaction volume in the microemulsion technique [11-16] or by controlling the particle`s surface free energy by in-situ surface modification during precipitation in the controlled growth reaction [16]. So, particle growth can be controlled and on the other hand the surface modification provides steric repulsive forces between the particles preventing agglomeration by van der Waals forces.

Both by the microemulsion and the controlled growth technique nanocrystalline powders can be prepared [11-16]. However these powders often show large aggregates so that the powders are mostly not redispersable. One reason responsible for the aggregation is the calcination technique (annealing) used in these works, because the surface modifying- or emulsifier layer on the particle surface is burned out and its passivating properties are lost. As a consequence of this the OH-groups on the now unprotected particle surfaces undergo condensation reactions resulting in interparticle bondings (aggregates). From this it can be concluded, that aggregation can be avoided, if the surface modifying layer can be maintained during the calcination step.

Our approach to fullfill this aim is the high temperature treatment of suspensions containing well dispersed amorphous particles at elevated pressure. During this treatment

the surface protective layer on the particles should not be destroyed to maintain its passivating effect and lead to aggregation free, redispersable particles. Previous works based on Yttria stabilized Zirconia showed that there is a strong dependency of the sintering temperature from the powder's aggregate size [17]. Whereas the densification temperature needed to compact ceramics made from powders of 15 nm primary particle size and aggregates > 300 nm was about 1600 °C the sintering temperature could be decreased to 1260 °C at aggregate sizes of 60 nm. So it can be expected that the sintering temperature for ZrO_2 ceramics prepared from aggregation free powders will be reduced below 1070 °C, the transformation temperature of monoclinic ZrO_2 to the tetragonale modification leading to compact, dense monoclinic ZrO_2 ceramics.

The goal of these works is the synthesis of nanocrystalline, redispersable (Y_2O_3-stabilized) ZrO_2 powders by high temperature/high pressure treatment of surface modified amorphous nanoparticles containing suspensions. This includes the evaluation of the effects of temperature and pressure on the crystallization behaviour as well as the powder characterization by X-Ray and HRTEM. Green parts of so obtained powders are to be prepared via colloidal processing as dry processing techniques are not practicable to obtain deffect-free green parts from nanopowders. Furthermore the sintering behaviour and the microstructure of sintered parts will be examined.

EXPERIMENTAL

Powder preparation

A solution of zircon-n-propoxide in ethanole containing 8 mole % of $Y(NO_3)_3$ (for the stabilized powders) was added dropwise to an aqueous ammonia solution containing 10 wt. % of the surface modifying agent, a 1 : 1 mixture of the emulsifiers Emulsogen OG® (Hoechst) and Tween 80® (ICI) [16], bifunctional amines, β-diketones or amino carbonic acids (e.g. β-Alanine) with respect to the oxide. The weight ratio of precursor- and water phase was 1. So prepared suspensions were treated at 230 °C and 50 bar for 3 hours (below the hydrothermal conditions for water: 374 °C, 218 bar) under nitrogen. The resulting powder was isolated by centrifuging and dried at 60 °C. The powders obtained by this procedure were characterized by HTEM, x-ray diffraction, C-analysis and zeta-potential measurements.

Powder processing

Colloidal suspensions were prepared by dispersing the powders in water at pH = 2. After powder addition the resulting suspensions were ultrasonical agitated for 10 min. To achieve a higher green strenth and to avoid cracks during drying, polyvinylic alcohole (3 wt. % with respect to the solid content) was added to the suspensions as a binder followed by ultrasonical treatment (5 min). The final solid content amounted to 50 wt: %. Afterwards green bodies were prepared by slip casting. After drying for 3 days in a controlled atmosphere the parts were sintered on air. The sintered parts were characterized by HRSEM and x-ray diffraction.

RESULTS AND DISCUSSION

Powder preparation

For the preparation of redispersable nanocrystalline powders by chemical synthesis both the microemulsion technique and the controlled growth technique are most promising because the surfaces of (amorphous) particles prepared by these techniques are protected either by emulsifiers or a layer of surface modifier avoiding agglomeration. In the present work the controlled growth technique was prefered because of the higher powder yield (110 g/l) compared with the microemulsion technique (12 g/l) [16]. In order to transform the obtained modified amorphous particles into nanocrystalline, redispersable particles, a following crystallization step should both avoid a degradation of the surface modifying layer and a particle contact. This can be done by high temperature/high pressure treatment of well dispersed suspensions containing the amorphous particles whereby the crystallization temperature can be reduced supported by high pressure rather than by calcination in a furnace whereby the protecting surface modifying layer is completely removed.

The synthesis of nano-scale modified particles containing suspensions was carried out by precipitation in presence of the surface modifying agent β-Alanine as described above. These suspensions were high temperature/high pressure treated. Systematic examinations on the temperature and pressure dependency of the crystallization behaviour of (Yttria-stabilized) ZrO_2, where the temperature was varied in 10 °C-steps from 100 °C to 230 °C and the pressure from 5 to 50 bar in 5 bar-steps, showed, that at a temperature of 230 °C and a pressure of 50 bar nanocrystalline particles can be obtained as to be seen in the x-ray diffraction diagram (fig. 1). in case of the stabilized powder there is a pure cubic modification of ZrO_2 to be found. The unstabilized powder consists mainly of a cubic and partly of monoclinic modification. This phase behaviour aggrees with [18], that below a critical particle size tetragonal material can be retained
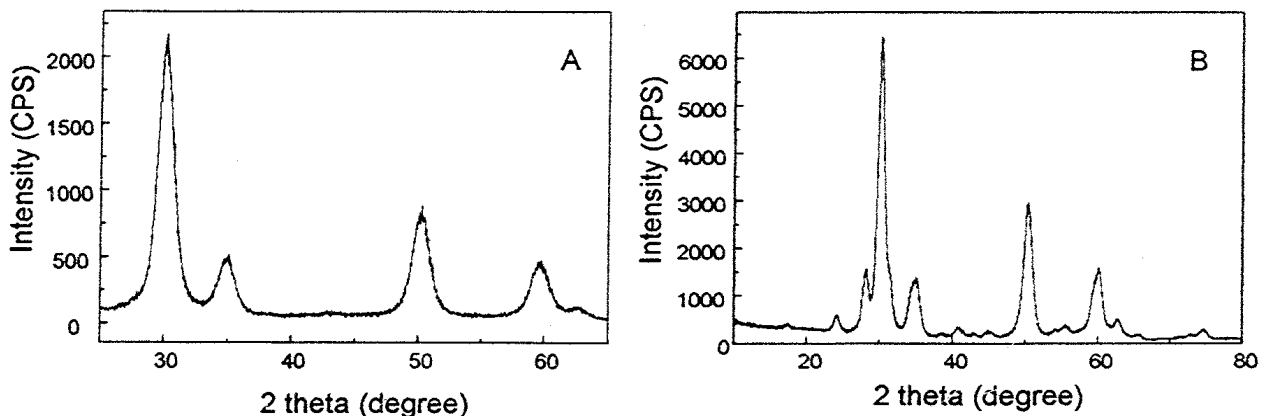

Fig. 1: X-ray diffraction of the nanocrystalline ZrO_2, A: 8 Y-ZrO_2,
B: unstabilized ZrO_2 after treatment at 230 °C and 50 bar for 3 h

The washed and dryed powders were analyzed by C and N analysis as well as by IR-spectroscopie to characterize the surface modification. From the ratio of the measured C-content (4.9 wt. %) and the N-content (1.9 wt. %) one can calculate from the molecular

coposition of β-Alanine used as surface modifier, that no degradation of the modifier happened and that the amount of β-Alanine on the powder surface is 0.0014 $^{mole}/_g$. As can be seen from IR-spectroscopie (fig.2) it can be assumed, that an esterfication of the carboxylic group with OH-groups on the powder surfaces took place, indicated by the peaks at 1550 $^1/_{cm}$ and 1450 $^1/_{cm}$, according to the model shown in figure 2.
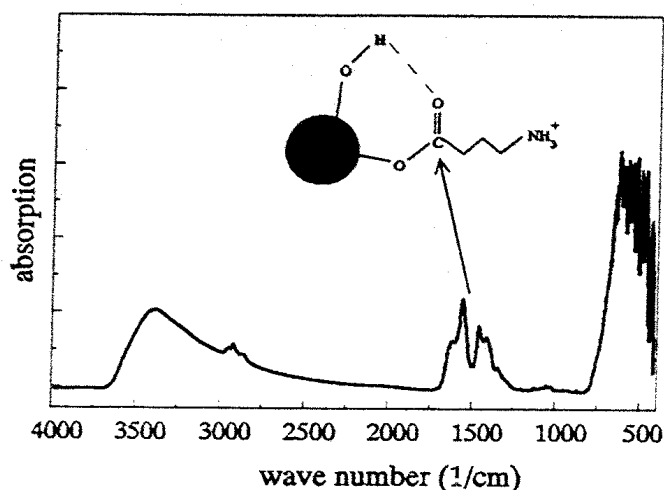

Fig. 2: IR-specrtum of β-Alanine-modified ZrO_2, crytallized at 230 °C and 50 bar

According to the concept described above, the nanocrystalline powders should show no aggregation due to the surface modification. To prove this, the powders were invastigated by HTEM as shown in figure 3. As can be seen from figure 3, the stabilized as well as the unstabilized powders can be well dispersed, the average particle size is between 5 and 10 nm.
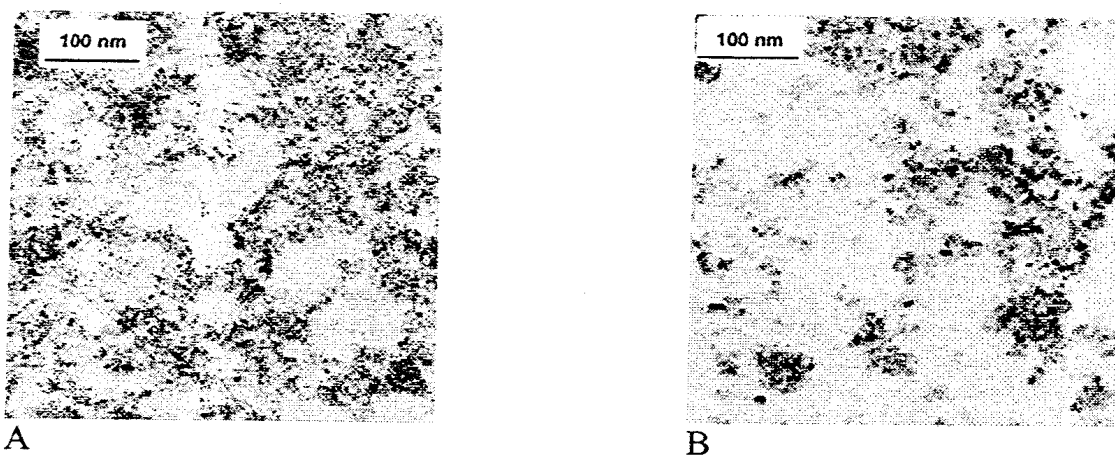

Fig.3:HRTEM-pictures of nanocrystalline powders, A: 8Y-ZrO_2, B: unstabilized ZrO_2 after treatment at 230 °C and 50 bar for 3 h

These results show, that the here prepared powders fullfill the essential prerequirements (nanocrystalline redispersable) for the fabrication of ceramics with

nanostructured microstructures. One other crucial point to be controlled is the processing technique.

Powder processing

Due to the small particle size resulting in short diffusion paths and higher capillary forces it can be expected, that green bodies from nano-scale powders can be densified at low temperatures, an increase of densification ratio/grain growth ratio can also be expected. As a consequence, very small grained ceramics can be obtained. However, this requires homogenous, deffect-free green bodies with a high packing density, which only can be prepared by colloidal processing.

In first experiments electrostatically stabilized colloidal suspensions of here prepared modified (stabilized) ZrO_2 have been investigated for preparing green parts by slip casting. Therefore it is necessary to find out at which pH maximum stabilization (highest zeta-potentiales) of the particles in suspension can be achieved. This has been done by pH-depending zeta-potential measurements as shown in figure 4. From figure 4 it is obviously, that the best stabilization can be reached in ph-regions between 2 and 4 or between 9 and 11 indicated by the highest zeta-potentials (> 30 mV and < -30 mV). From figure 4 it can be seen that the surface modification influences the zeta-potential by shifting the pH_{iep} from pH = 5 for unmodified stabilized ZrO_2 , obtained after basic deesterfication and removal of the surface modifyer by washing with water, to pH = 8 for modified stabilized ZrO_2. Furthermore a better stabilization can be achieved due to the surface modification because of the higher zeta-potential, e.g. 33.6 mV for the modified compared to 22.8 mV for the unmodified powder at pH = 4.
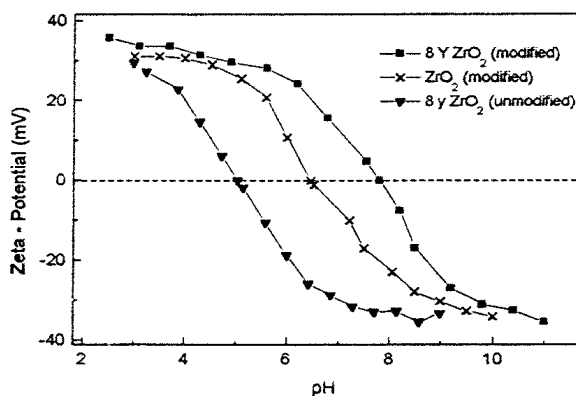

Fig. 4: pH-depending zeta-potential measurements of modified stabilized and unstabilized ZrO_2 and unmodified stabilized ZrO_2 (Titration: HCl vs. NaOH)

As, on the one hand, a good stabilization and dispersion of the surface modified powders can be achieved at pH = 2 due to the high zeta-potential of > 30 mV and, on the other hand the acidic pH is compatible with the chosen binder system, colloidal suspensions of the stabilized as well as the unstabilized ZrO_2 powders with solid contents of 50 wt. % were prepared as described above. The particle size distributions in the resulting suspensions were characterized by laser backscattering measurements.

According to these measurements (fig. 5) the particles are well dispersed in the colloidal suspensions with 90 % of particles smaller than 30 nm.
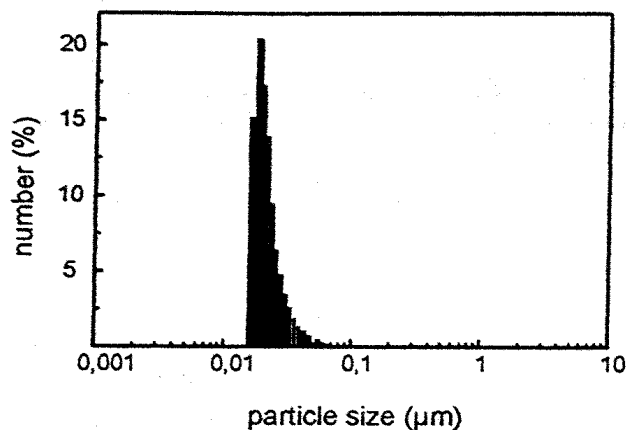

Fig. 5: Particle size distribution of an aqueous ZrO_2 suspension at pH = 2

These colloidal suspensions were used for slip casting experiments. After drying in a controlled atmosphere, green bodies with 45 % densities were obtained. According to the small primary particle size and the good state of dispersion in the colloidal suspensions used, the green bodies are distinguished by a narrow pore size distribution measured by BET-method with pore diameters between 2 and 5 nm (fig. 6). From the pore size distribution it can be concluded, that the green bodies possess a homogenous microstructure, too.
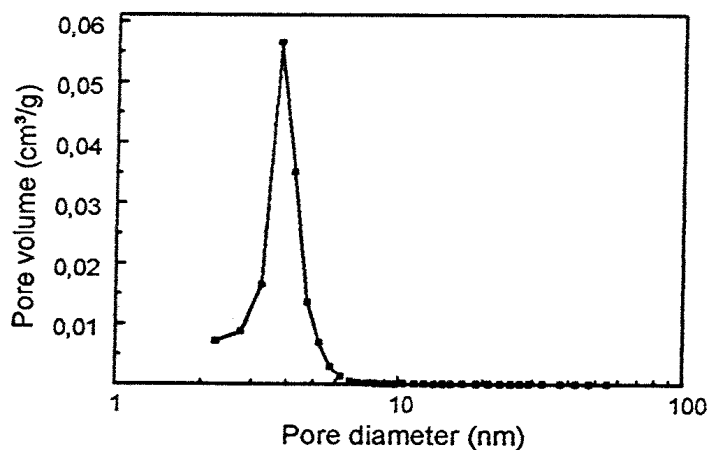

Fig. 6: Pore size distribution of slip cast green bodies measured by BET

The homogenous mcrostructure in combination with the small particle size and the narrow pore size distribution should make it possible to densify the green parts at low sintering temperatures and low sintering temperatures in turn are necessary to decouple densification and grain growth and to obtain dense ceramics with a nanostructured microstructure.

In order to prove the densification behaviour, sintering experiments on stabilized and unstabilzed ZrO_2 green bodies were carried out. These experiments showed, that a sintering temperature of 1030 °C is sufficient to obtain 8 Y-ZrO_2 ceramics with densities > 95 %. HSEM investigations of the sintered microstructure indicated grain sizes between 50 nm and 100 nm (fig. 7A). In case of the unstabilized ZrO_2 a sintering temperature of 1060 °C was needed to achieve densities above 95 %. Due to the high sintering activity it was possible to prepare dense unstabilized ZrO_2 ceramics that could be densified below the transformation temperature of the monoclinc to the tetragonal modification. Here, the average grain sizes are even smaller than 50 nm as to be seen in fig. 7B.
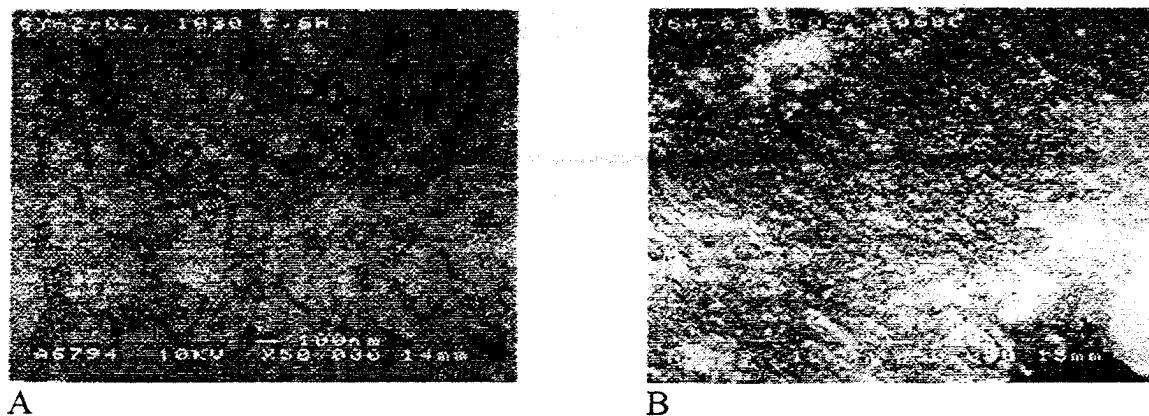

A   B

Fig. 7: Microstructures of sintered ZrO_2 ceramics; A: 8 Y-ZrO_2, B unstabilized ZrO_2

For grain growth is a diffusion controlled process, the driving force for this process at a given temperature is determined by the curvature of the present grain boundaries. Therefore, the initial grain growth rate of ceramics with nano-scale microstructures may be comparatively high as observed in present work on nanocrystalline (stabilized) ZrO_2.

CONCLUSIONS

It could be shown that dense, nanostructured ceramics with grain sizes below 50 nm can be prepared by combining a surface free energy controlled powder synthesis technique with a colloidal processing step. Due to the low sintering temperatures it was possible to densify unstabilized (monoclinic) ZrO_2 below its transformation temperature. The evaluation of the mechanical properties of so prepared monoclinic ceramics will be matter of further investigations. Furthermore the low sintering temperature offers a broad field of new applications as for example new material combinations or cofiring techniques.

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