

PREPARATION OF MONODISPersed ZIRCONIA POWDERS FROM SOLUTION

G. Rinn, H. Schmidt
Fraunhofer-Institut für Silicatforschung
Neunerplatz 2
D-8700 Würzburg
Federal Republic of Germany

ABSTRACT

Conditions for the preparation of zirconia powders from solutions were investigated. Variations of reaction parameters, e. g. concentration of the precursor, ratios of water, nitric acid, acetylacetone and hydroxypropylcellulose, sequence of addition and temperature, led to the precipitation of monodispersed particles. According to an increasing concentration of acetylacetone, the mean diameters rose from about 600 nm up to 2.5 μm . Calcination of the dried amorphous powders caused transformations to tetragonal zirconia in the range of 400 - 500°C and to monoclinic zirconia at about 700°C and is accompanied by a weight loss of 42 - 44 % and a linear shrinkage of up to 40 %.

INTRODUCTION

The chemical synthesis of fine powders (e. g. ZrO_2) is a topic of modern ceramic research. Zirconia powders with particle sizes ranging from 1 - 100 nm could be achieved through the pyrolysis of zirconium alkoxides⁽¹⁾ or the hydrothermal treatment of zirconia gels⁽²⁾. The hydrolysis of zirconium alkoxides in diluted solutions yields, under appropriate reaction conditions, monodispersed spherical particles with mean diameters in the range from about 50 - 500 nm⁽³⁾. Larger spheres (15 - 1000 μm) could be prepared from emulsified aqueous zirconia sols⁽⁴⁾. However, the reproducible preparation of monodispersed zirconia powders with different particle sizes remains problematic. An essential condition for the development of monodispersed particles in solutions is a homogeneous nucleation and further growth with small supersaturation; that means, the spontaneous precipitation during the addition of water to zirconium alkoxides must be avoided. This could be attained through the use of acids⁽⁵⁾ or of complexing agents, e. g. acetylacetone⁽⁶⁾. A further condition for the growth of monodispersed particles is the hindrance of agglomeration. A steric stabilization of gro-

wing particles could be achieved through the addition of surface-reactive polymeres, e. g. hydroxypropylcellulose⁽⁷⁾. The aim of this work was the development of a method for the preparation of monodispersed zirconia powders with different particle sizes, with respect to some growth-controlling parameters (concentrations, complexing agent, stabilizer, water, acid, temperature) and the characterization of the reaction products.

EXPERIMENTAL PROCEDURE

Test Series

First investigations to the hydrolysis of solutions of zirconium-isopropoxide in ethanol in the presence of hydroxypropylcellulose (Kluacel EF, Fa. Hercules) as a stabilizer, acetylacetone as complexing agent and nitric acid led, under appropriate reaction conditions and concentrations, to the precipitation of monodispersed particles.

To enlighten the influence of the different compounds, the following parameters were varied in some test series:

- Zirconium-isopropoxide was used with concentrations of 1.0 and 1.5 mol/l in ethanol.
- Hydroxypropylcellulose (HPC) was added as a 5 wt% ethanolic solution in concentrations of 0.0, 12.5, 25.0 and 37.5 g/mol Zr. The same total volumes were adjusted through the addition of ethanol.
- The concentration of acetylacetone was varied in the range from 0 - 1 mol/mol Zr with increments of 0.125 mol.
- Water and nitric acid were added as a mixture; the concentrations were adjusted for water to 2.0, 2.5, 3.0, 4.0 and 6.0 mol/mol Zr and for nitric acid to 0.00, 0.25, 0.50, 0.75 and 1.00 mol/mol Zr.
- The reactions were performed at room temperature, 40°C and 60°C.

Preparation of monodispersed zirconia powders

A method for the preparation of monodispersed zirconia powders with different mean diameters could be developed with respect to the above mentioned investigations (Fig. 1).

40 ml solutions of zirconium-isopropoxide with concentrations of 1 mol/l in ethanol were mixed with 20 ml of a 5 wt% ethanolic solution of HPC and 10 ml ethanol. Subsequent, 1.2, 1.6, 2.0 and 2.4 g acetylacetone, corresponding to 0.30, 0.40, 0.50 and 0.60 mol acacH/mol Zr, and a mixture of 2.1 ml 65 % nitric acid and 0.6 ml water were added. The solutions were stirred for homogenization and tempered at 40°C in a water bath. The precipitated powders were named, according to the concentration of acetylacetone, as Zr30, Zr40, Zr50 and Zr60.

The isolation of the particles in the suspensions to monodispersed powders required a considerable effort, because of the non-quantitative reaction, which means, mono- or oligomeric species were still in solution. Typical reaction yields were in the range

and polar organic solvents, whereas apolar solvents in excess caused insolubility of the HPC and accordingly agglomeration and flocculation of the particles.

This problem could be solved with the following procedure: 50 ml petroleum ether were dropped to the suspensions under stirring. The particles were centrifuged, redispersed in a mixture of 25 ml ethanol and 20 ml petroleum ether and mixed with further 30 ml petroleum ether under ultrasonic agitation. Spray drying of the suspensions yielded powders free of hard agglomerates.

RESULTS AND DISCUSSION

Conditions for the precipitation of monodispersed particles

Visual and light-microscopic evaluations of the reaction products enabled the development of conditions for the preparation of monodispersed particles with different mean diameters. The influences of single reaction parameters could be described as follows:

- Zirconium-isopropoxide should be used with a concentration of 1 mol/l in ethanol; higher concentrations caused the formation of agglomerates.

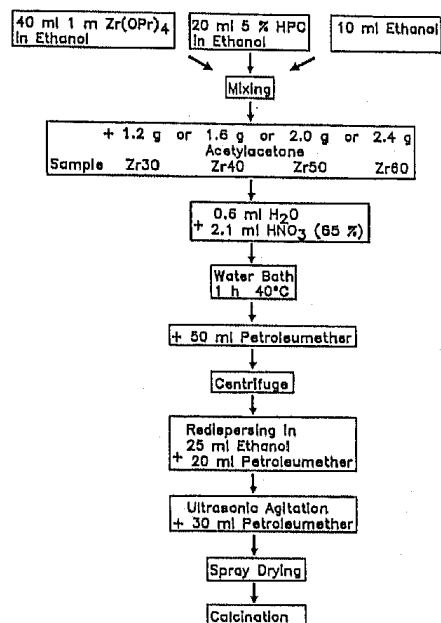


Fig. 1: Schematic diagram of zirconia powder processing.

- 25.0 g HPC/mol Zr were sufficient for the hindrance of agglomeration of particles.
- The hydrolysis of the alkoxide without acetylacetone (acacH) led to clear solutions or irregular precipitates, dependent on the concentration of nitric acid. The addition of acetylacetone enabled the preparation of spherical particles; the mean diameters ranged from about 200 nm to 10 μm . Monodispersed suspensions could be obtained up to 3 μm , corresponding to 0.6 mol acacH/mol Zr. Larger particles were agglomerated, because of sedimentation and compaction during the growth.
- The preparation of monodispersed particles required nitric acid in concentrations of 0.75 or 1.00 mol/mol Zr. Smaller amounts caused clear solutions, gels or precipitates in dependence of the reaction conditions. 2.00 - 2.25 mol H_2O /mol Zr were sufficient for the precipitation of spherical particles; higher concentrations of water resulted in increasing particle sizes and agglomeration as well as in a lower yield.

Characterization of the Zirconia Powders

The powders Zr30, Zr40, Zr50 and Zr60 were characterized, using electron-microscopy, thermal analysis, X-ray-diffraction and infrared-spectroscopy after different calcination temperatures:

- Scanning Electron Microscopy

Dried and at 700°C calcined powders were investigated by scanning electron microscopy (Fig. 2 - 9): According to the increasing concentration of acetylacetone from Zr30 to Zr60, the mean diameters of the particles rose from about 0.6 μm to 1.0 μm , 1.5 μm and 2.5 μm . Smaller particles and agglomerates within the powders could be attributed to the precipitation of dissolved material during the washing process; primary intergrown particles, especially in Zr50 and Zr60 show a more twinned structure. Calcination of the powders caused a linear shrinkage of the particles up to 40 % and led to mean diameters ranging from 0.4 μm to 1.5 μm .

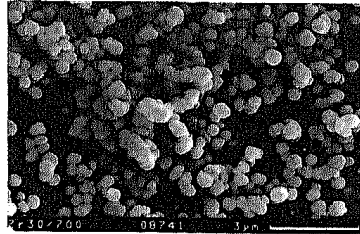
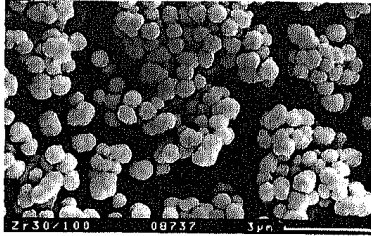
- Thermal Analysis

Thermogravimetry (TG) and Differential Thermal Analysis (DTA) indicated a rather similar behaviour of the four powders (Fig. 10 - 13). A continuous weight loss of about 40 % and two exothermal reactions occurred in the range of 200 - 400°C, attributable to the decomposition of nitrates and volatile organic compounds. The thermal decomposition of the zirconium-acetylacetone-complexes led to the formation of carbon, which started to burn out at about 650°C in air. Dependent on the total amount of carbon, the different particle sizes and according to the heating rate of 20°C/min, the burnout-interval changed from 650 - 700°C to 650 - 900°C. Additional experiments with constant calcination temperatures showed a complete burnout of carbon at 700°C in all powders and a total weight loss in the range of 42 - 44 %.

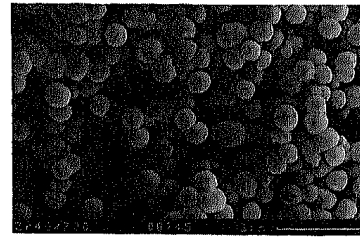
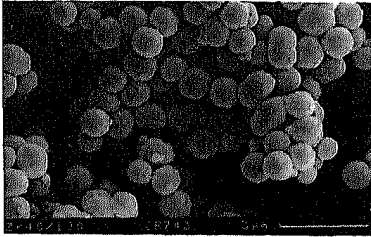
100°C

700°C

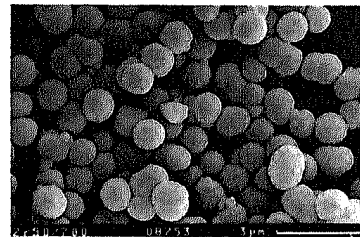
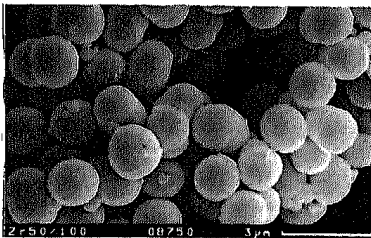
Zr30



Zr40



Zr50



Zr60

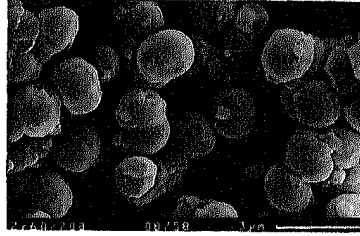


Fig. 2 - 9: SEM-micrographs of dried and calcined zirconia powders Zr30, Zr40, Zr50 and Zr60.

- X-Ray Diffraction

XRD-diagrams (Fig 14 - 17) of Zr30 and Zr60 showed amorphous powders up to 400°C. Crystallization to metastable tetragonal zirconia occurred between 400°C and 500°C. The transformation to the stable monoclinic phase started at about 700°C and seemed to be related to the burnout of carbon; Zr60 with the larger burn-out-interval showed at 700°C a greater amount of residual tetragonal zirconia ($2\theta = 30^\circ$). Calcination at 900°C caused sharpening and increasing intensities of the peaks of monoclinic and a further decrease of tetragonal zirconia.

- Infrared Spectroscopy

IR-spectra of dried powders of Zr30 and Zr60 (Fig. 18 - 19) indicated the presence of hydroxyl groups ($3000 - 3800 \text{ cm}^{-1}$), nitrates (1380 cm^{-1}) and the acetylacetonate-complex, with the main absorption bands in the range from $800 - 1700 \text{ cm}^{-1}$ (Fig. 20). Broad bands from $300 - 700 \text{ cm}^{-1}$ seemed to be related to structures similar to zirconia (Fig. 21). The IR-spectra showed no absorption bands, which singularly corresponded to HPC (Fig. 19), indicating that it only could be absorbed in small quantities on the particle surfaces and was not incorporated inside the particles. Calcination of the powders caused a decrease of hydroxyl groups, nitrates and organic compounds and an increasing absorption in the range of $300 - 800 \text{ cm}^{-1}$, leading finally to

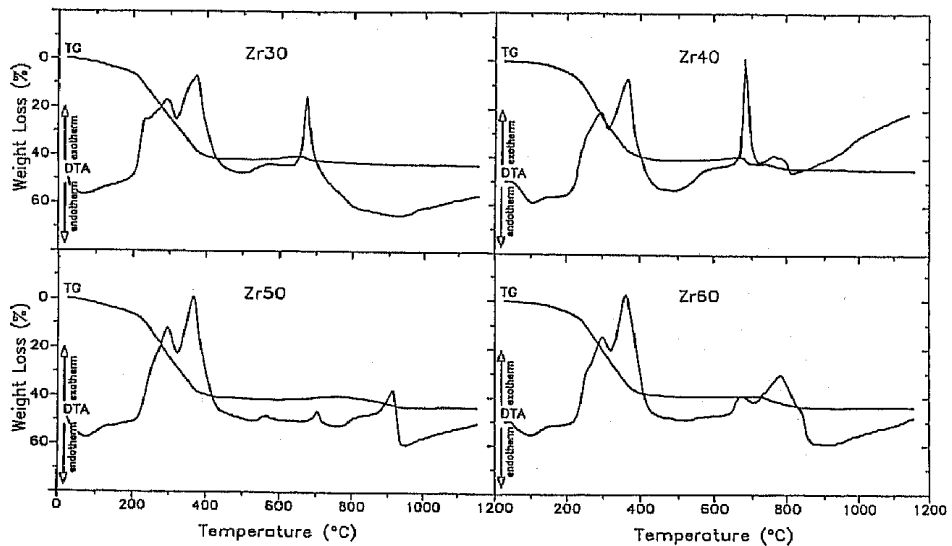


Fig. 10 - 13: Thermal analysis of the zirconia powders.

the spectrum of zirconia at 700°C. Corresponding to the burnout of carbon, these spectra showed the absorption band of adsorbed carbon-dioxide at about 2340 cm⁻¹; calcination at higher temperatures resulted in the disappearance of this band.

CONCLUSIONS

A new method for the controlled synthesis of zirconia particles has been developed; the dominant size-determining parameter is the concentration of acetylacetone, whose increase causes increasing mean diameters from about 200 nm to 10 μm. Further work will be done with respect to improved techniques for the precipitation of particles and the isolation of powders. Such monodispersed and monosized powders in the total range of particle sizes could be very suitable model substances for densification and sintering experiments.

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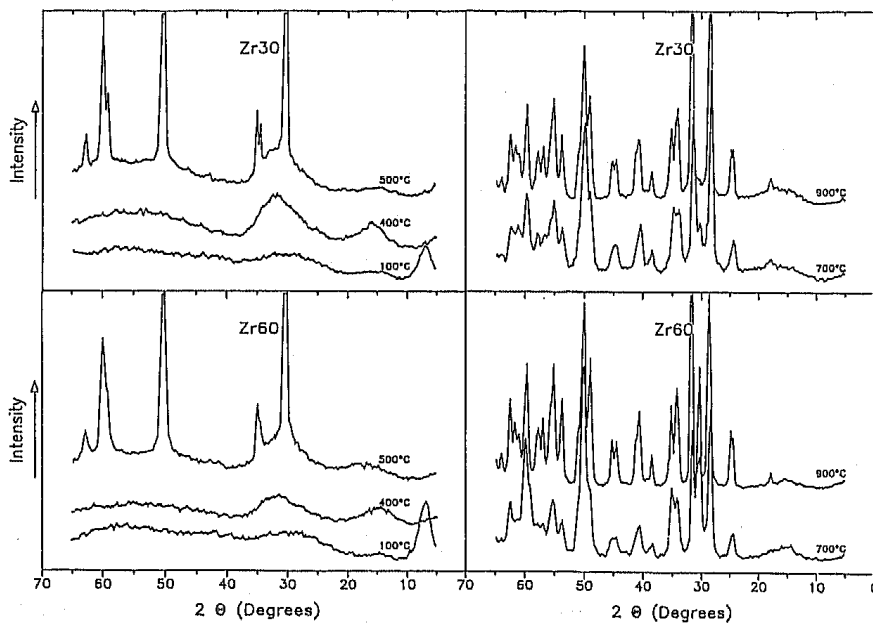


Fig. 14 - 17: X-ray diffraction pattern of dried and calcined powders Zr3O and Zr6O.

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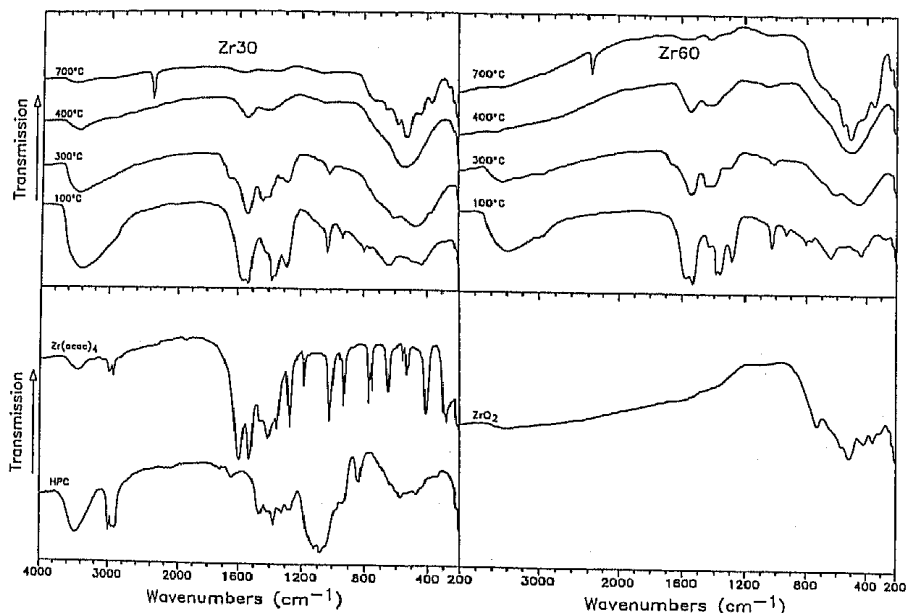


Fig. 18 - 21: Infrared-spectra of dried and calcined powders Zr30 and Zr60, as well as reference spectra of zirconium-acetylacetonate, hydroxypropylcellulose and monoclinic zirconia.

Volume 1

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