

PREPARATION OF Y-DOPED ZIRCONIA BY EMULSION TECHNIQUE

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ABSTRACT

Spherical Y-doped zirconia powders have been prepared from water in oil-emulsions of acid stabilized aqueous sols. The precipitation of hydroxides inside the droplets was achieved by an ion exchange process between the aqueous phase and an anion exchange resin, using a phase transfer catalyst as a carrier for the anions through the organic solvent. Azeotropic distillation of the water caused a densification to spherical amorphous particles. Filtration, drying and calcination led to the formation of a tetragonal zirconia powder. Isostatically pressed powder compacts sintered at 1650 °C to theoretical density.

INTRODUCTION

Ceramic powders with definite particle size distributions and shapes are of increasing interest for the preparation of high performance ceramics.

Many procedures for the preparation of fine spherical powders with a narrow size distribution have been described, e. g. by the synthesis from solution (1-3) or from gas phases (4); but it is very difficult to achieve defect free microstructures from monosized powders (5). Serious disadvantages of some of these processes are their low yields because of extremely low concentrations of the precursor in the gas or liquid phase, the expensive raw materials (e. g. alkoxides in organic solvents) and difficulties in the preparation of multicomponent systems.

The use of an emulsion technique with an aqueous phase allows the introduction of inorganic salts or sols, almost independent on composition.

Solid particles can be formed from emulsions by the rapid evaporation of the water from salt solutions (6-7) or the precipitation of hydroxides, e. g. by bubbling gaseous ammonia through the reaction medium (8). But in this cases the thermal decomposition of the metal- or ammoniumsalts in the particles causes a large weight loss and a disintegration of the spheres or large intragranular pores.

An extraction of acids or anions of acid salts from the aqueous phase can be performed by the addition of oil-soluble amines to the emulsion (9); but in a batch process a large excess of amines is necessary to achieve a complete extraction. Furthermore the employed weak bases cannot transform neutral salts to the corresponding hydroxides.

A possible route to avoid these disadvantages seems to be the use of oil soluble strong bases, e. g. quaternary alkylammoniumhydroxides. Alkylammonium-cations are used as phase transfer catalysts in organic chemistry; they are able to carry anions through an organic solvent and to exchange them at a oil-water phase boundary. Therefore it should be possible to use a phase transfer catalyst as a carrier for anions between an anion exchange resin as a base reservoir and the emulsified aqueous phase. Consequently catalytic concentrations of this compound should be sufficient to achieve a complete exchange of the anions and the precipitation of the hydroxides. The aim of this investigations was to work out an experimental procedure for the preparation of ceramic powders and to test the process with Y-doped zirconia as a model.

EXPERIMENTAL

Aqueous zirconia sols were prepared by the acid hydrolysis of zirconiumpropoxide for these first investigations, but their preparation from aqueous solutions of zirconiumsalts is possible, too.

109.2 g of a solution of zirconium-n-propoxide in 2-propanol (75 wt%) were dissolved in ethanol and a mixture of 22 ml nitric acid (65 wt%) and 25 ml water was added. The molar ratio of zirconium to nitrate was about 1. Double evaporation of the solvents at 60 °C and redissolving of the residue in water resulted in a clear aqueous zirconia sol which is stable for several days. The use of nitric acid as a peptizing agent enables the preparation of sols with a concentration of up to 50 wt% with respect to zirconia. 5.76 g yttriumnitrate-hexahydrate were dissolved in water and added to the zirconia sol to achieve tetragonal zirconia, stabilized with 3 mol% yttria as the final product. The total volume of the precursor was adjusted to 100 ml by the addition of water.

The aqueous sol was emulsified in petroleumether (boiling range 50 - 70 °C), using Emulsogen OG (Fa. Hoechst) as an emulsifier. The resulting droplet size distribution was in the range of about 0.5 - 5 μm.

1.5 g didodecyldimethylammoniumbromide were dissolved in 10 ml 1-octanol and added to the emulsion. After stirring for a few minutes, the emulsion was put in an ion exchange column, filled with 500 g Dowex 1x8 (Fa. Dow Chemical), a strongly basic ion exchange resin in the basic form. The completion of the exchange process was controlled with pH- and nitrate-indicatorsticks. According to the flow rate of 50 - 200 ml/min a single or double passage of the emulsion through the column was sufficient to achieve an approximately complete exchange (pH 7 - 8, < 50 mg NO₃ /l).

The removal of the water from the resulting hydroxide droplets was performed by azeotropic distillation and its separation with a Dean Stark moisture trap. The addition of 10 ml 1-butanol increased the concentration of water in the gaseous phase from about 5 - 20 wt%.

The water-free hydroxide particles were filtered off, re-dispersed in petroleum ether, filtered again, dried at 100 °C and calcined at different temperatures for 2 h. The resulting powders were examined, using infrared spectroscopy, thermal analysis, X-ray diffraction and scanning electron microscopy. In addition the specific surface areas and the densities of green and sintered compacts were investigated in relation to different calcination temperatures.

RESULTS AND DISCUSSION

The data described in the experimental part show the possibility to prepare zirconia powders with the proposed technique. Standard characterizations were carried out to demonstrate the processing properties of the powders.

- Infrared spectroscopy and thermal analysis

The processing of the inorganic zirconia sol was expected to lead to a powder almost free of organics and salts and therefore a small weight loss during calcination. The thermal analysis (Fig. 1) shows a total weight loss of about 22 wt% and infrared spectra indicated the presence of organic compounds (peaks at 2900 - 3000 cm^{-1} and 1200 - 1700 cm^{-1}) and some nitrates (peak at 1380 cm^{-1}) up to 250 °C.

The emulsifier and the phase transfer catalyst are surface active agents and probably strongly adsorbed at the zirco-

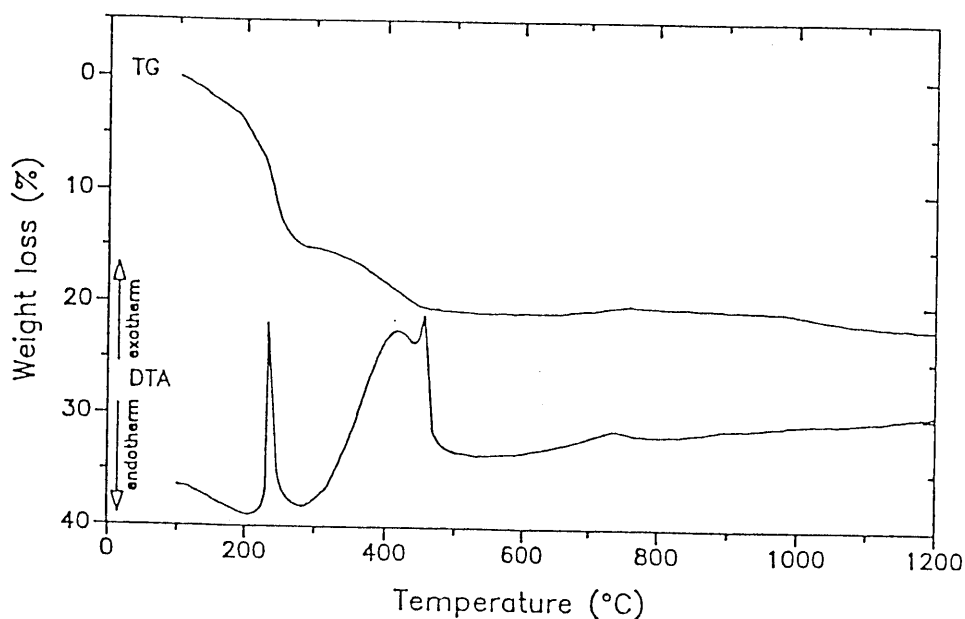


Fig. 1: Thermal analysis of the zirconia powder.

nia particles, so that simple washing processes are not sufficient for their complete elimination.

The spontaneous exothermal reaction and weight loss at about 240 °C can be related to the decomposition of the adsorbed alkylammonium salt and the broad exothermal peak in the range 300 - 450 °C to the degradation of the emulsifier. The small exothermal peak without any weight loss at 460 °C indicates the crystallization of zirconia, as shown later from X-ray data. At 500 °C the powder was almost free of organics, nitrates and hydroxides and no remarkable weight loss occurred up to 1200 °C.

- X-ray diffraction

X-ray diffraction pattern (Fig. 2) show an amorphous material after drying at 100 °C and tetragonal zirconia at 500 °C. The broad peaks indicate very small or distorted crystals; further heating resulted in a sharpening and increasing intensities of the peaks, but no monoclinic zirconia occurred.

In general pure amorphous zirconia from gels or hydroxides crystallizes first metastable in the tetragonal high temperature form, but transforms into the stable monoclinic form below 1000 °C. The lack of phase transformation in this case demonstrates a homogeneous distribution of the yttria in the zirconia, causing the stabilization of the tetragonal form at room temperature.

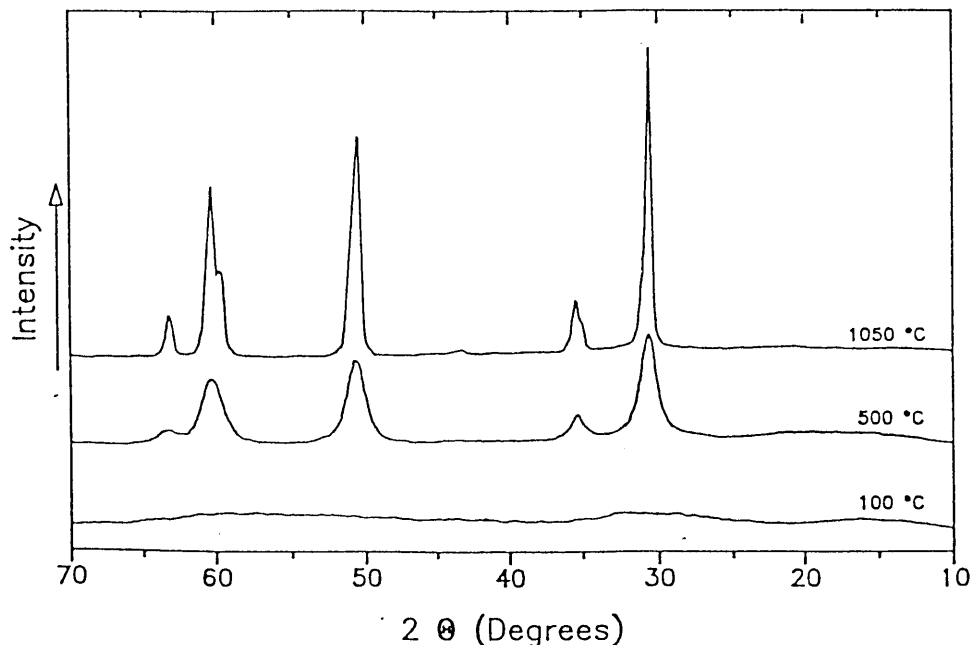


Fig. 2: X-ray diffraction pattern of dried and calcined zirconia powders

- Scanning electron microscopy

Scanning electron micrographs of the dried powder show almost perfect spheres with a size distribution of about 0.3 - 3 μm (Fig. 3 - 4). The calcination up to 850 °C led to a linear shrinkage of about 50 % (Fig. 5 - 6). Even in this sample no hard agglomerates could be detected. This is attributed to the adsorption of the emulsifiers and the phase transfer catalyst at the particle surfaces, as detected by infrared spectroscopy. Especially at temperatures, where OH-groups on surfaces disappear (< 400 °C), sol-gel powders tend to form strong agglomerates by condensation processes. The adsorption of organic molecules is considered as the reason for the lack of agglomeration in this case. Some fragments indicate the formation of hollow spheres only from very large droplets and demonstrates the needs for emulsions with a smaller maximum droplet size. At higher temperatures a crystal growth occurred and caused a substructure of the particle surfaces and the formation of some agglomerates.

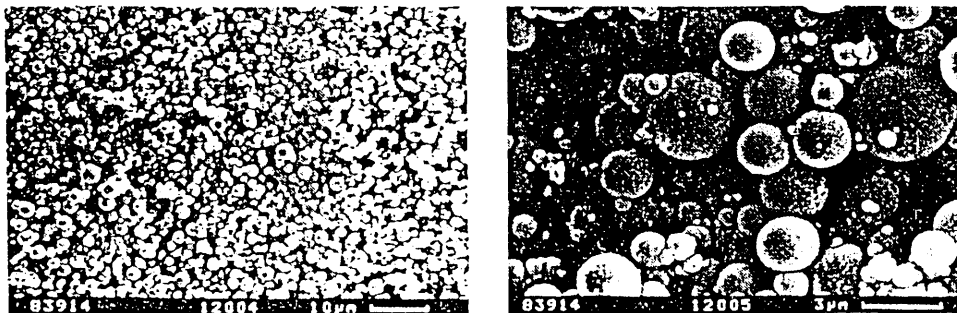


Fig. 3 - 4: SEM-micrographs of the dried zirconia powder.

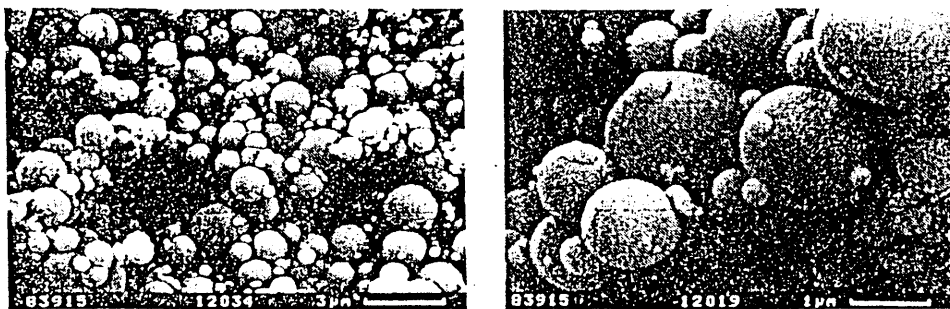


Fig. 5 - 6: SEM-micrographs after calcination at 850 °C.

- BET-surface area, densification and sintering

High green densities of powder compacts require the processing of powders free of internal pores and hard agglomerates. Therefore the specific surface areas after calcination in the range 650 - 1050 °C were determined. The BET-surfaces of the powders decreased between 650 °C and 850 °C from about 4.6 m²/g to 1.8 m²/g and remained almost constant at higher temperatures (Fig. 7).

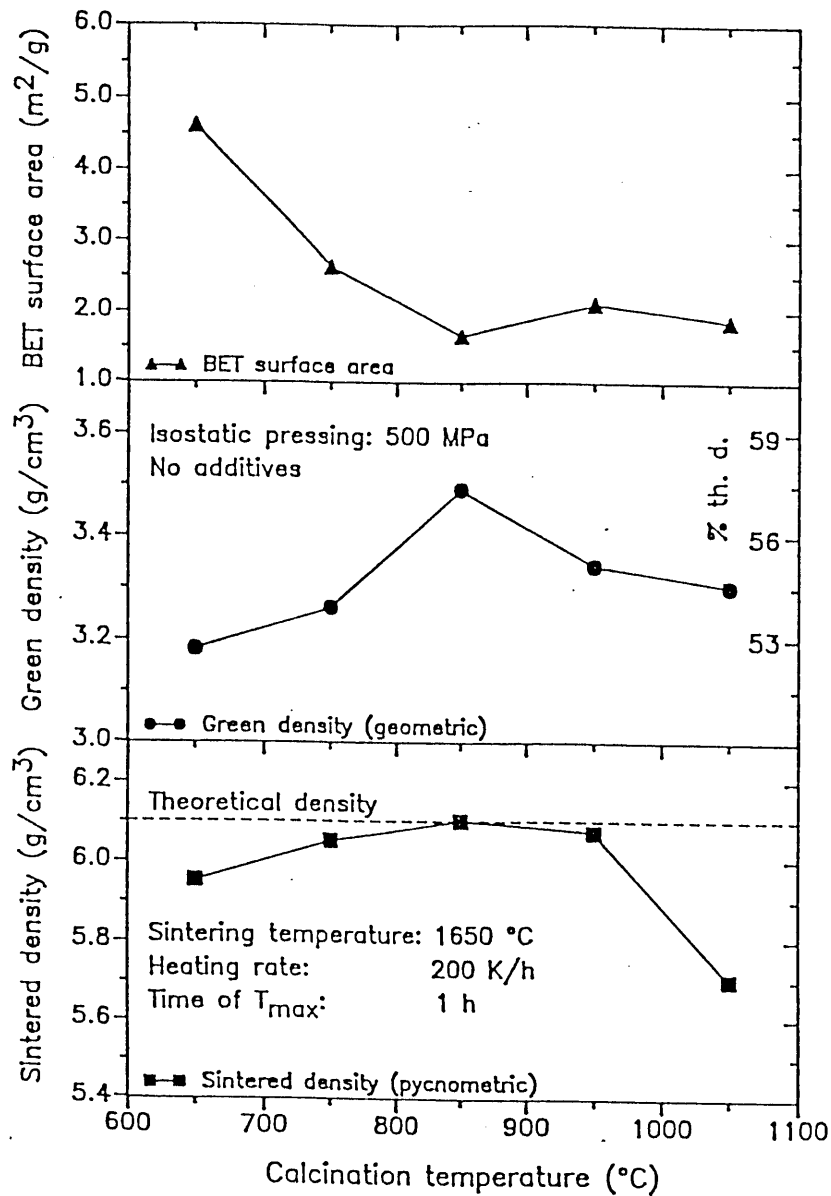


Fig. 7: BET-surface areas, green and sintered densities as a function of calcination temperatures.

Isostatic pressing of the powders at 500 MPa without any additives and process optimization resulted in compacts with green densities in the range 3.2 - 3.5 g/cm³ (Fig. 7). The highest density (57 % th. d.) was achieved with the powder calcined at 850 °C.

The sintered densities of the powders calcined at different temperatures is shown in Fig. 7, too. Only the 850 °C calcined powder resulted in a sintered body with 100 % theoretical density. Powders calcined at lower temperatures led to lower green densities by the standard dry pressing process and as a consequence to remaining pores in the sintered body. Calcination above 850 °C caused the formation of aggregates, which, since no milling was performed, were transferred into the green body, leading to lower densities in the sintered body, too.

- High temperature dilatometry

The sintering behavior of the powder calcined at 850 °C was investigated by dilatometry (Fig. 8). A powder compact with 55 % theoretical density was annealed to 1580 °C with a heating rate of 1 °C/min. Sintering started between 1000 and 1050 °C and, up to 1580 °C (the end point of the dilatometer), the compact densified to 97 % theoretical density. This confirms the observed formation of agglomerates after calcination at 1050 °C, because it is just the temperature, where the sintering started. The very broad sintering interval demonstrates on the one side the high sintering activity of the powder, but on the other side also the needs for smaller maximum particle sizes, to achieve theoretical densities of compacts at lower temperatures.

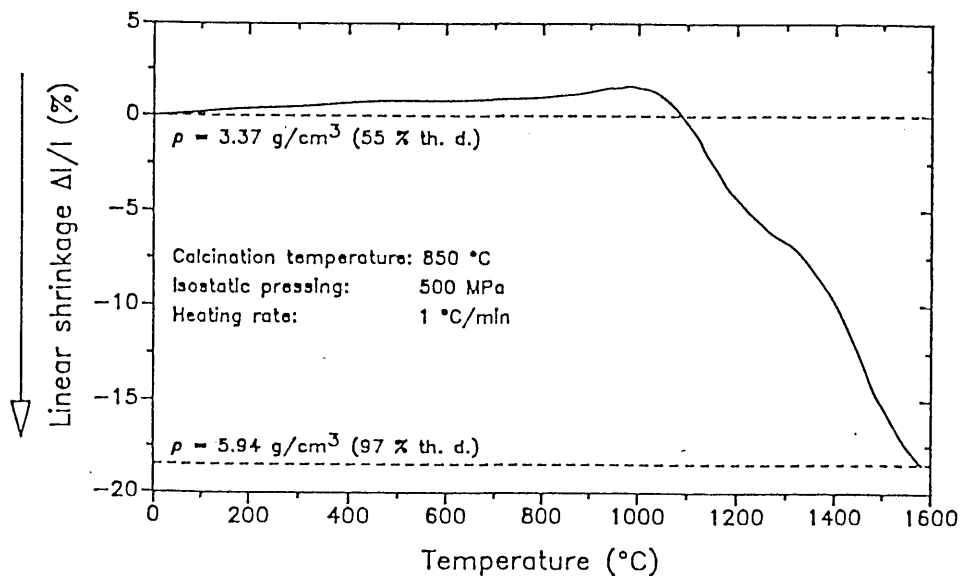


Fig. 8: High-temperature dilatometry of a powder compact.

CONCLUSIONS

The described combined emulsion- and ion-exchange-process for the synthesis of spherical ceramic powders offers some advantages in relation to other preparation techniques:

- It is possible to use aqueous sols and/or inorganic salts as precursors for a sol-gel-like process within droplets.
- Multicomponent systems can be realized by the use of mixtures of soluble precursors.
- Droplet sizes and distributions can be defined by mechanical and chemical parameters; e. g. shear rate and the properties of the solvent and the emulsifier.
- The powders show a relative high sintering activity without intense milling.

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