

Manufacturing and Properties of ZTA-Ceramics with Nanoscaled ZrO_2

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Abstract

Zirconia toughened alumina (ZTA) was produced by adding 5 Vol.% nanoscaled zirconia with a primary particle size of 12 nm. It was shown that mechanical properties were significantly improved, compared to pure alumina ceramics and conventional zirconia toughened alumina with microscaled zirconia. This improvement was achieved due to a strong inhibition of grain growth of the alumina phase by the homogeneously dispersed nanoscaled zirconia. Compared to pure alumina ceramics this led to an increase of strength of 70 %. In addition, the standard deviation of these strength measurements was much lower. The fracture toughness increased by 15 % and hardness remained as high as that of pure alumina.

Key words: Zirconia-toughened-alumina, ZTA, nanoscaled zirconia

Introduction

During the last several decades, a lot of research work has been done focusing on the property improvement that results when alumina and zirconia ceramics are combined. This type of material is referred to as Zirconia Toughened Alumina (ZTA). Studies were carried out with unstabilized, monoclinic zirconia as well as stabilized, tetragonal ZrO_2 . For instance, zirconia concentrations of up to 20 Vol.% were tested in [1]. Claussen [1] has shown that the fracture toughness, K_{IC} , of alumina can be significantly increased by the addition of ZrO_2 . The addition level of zirconia resulting in the maximum K_{IC} value was found to depend on particle size, from 4 Vol.% with 5,4 μm particles to 15 Vol.% with 1,25 μm particles. Claussen also found in all experiments that strength decreases compared to pure alumina ceramic when zirconia particles are added. Decrease in strength was higher for the larger zirconia particles. In contrast to this, other works found an increase in strength resulted from using zirconia

particles smaller than $< 1 \mu m$ [2, 3] Langer and Hirlinger [4] showed that grain growth of the alumina matrix can be limited by the addition of 5 Vol.% ZrO_2 . Excellent wear resistance was determined to be the major advantage of ZTA ceramics [5].

The scope of the present study was to examine whether the mechanical properties of ZTA ceramics could be improved by the addition of very fine "nanoscaled" zirconia. Results for the nanoscaled ZrO_2 („n-ZTA“) were compared to pure alumina ceramics and to conventional ZTA with microscaled ZrO_2 („m-ZTA“). In this text we understand "nanoscaled" particles to have, when dispersed in water, average particle sizes are in the colloidal range, i.e. between 1 and 200 nm. Significantly larger particles are referred to as microscaled.

Experimental

Raw Materials

A high purity alumina powder (CT3000 SG by *Almatis GmbH*, 99,8 % Al_2O_3) with an average particle size of 0,8 μm and specific BET surface of 7,5 m^2/g (BET) [6] was used as the basic component for all samples.

The nanoscaled ZrO_2 was added in form of a stable suspension (VP Disp. W 2650 X by *Degussa AG*). The suspension contains unstabilized zirconia that is produced by a high temperature flame synthesis method known as the AEROSIL® process [7]. The ZrO_2 particles have an average primary particle size of 12 nm. As part of the flame process, the primary particles are sintered together into aggregates (Fig. 1). The suspension was prepared by applying strong shear forces to a mixture of zirconia and water. By doing this, an average aggregate diameter of less than 100 nm was obtained. The suspension had a solid content of 50 mass % ZrO_2 and low viscosity (< 2000 mPas, measured by Brookfield at 50 rpm, 20°C) [8].

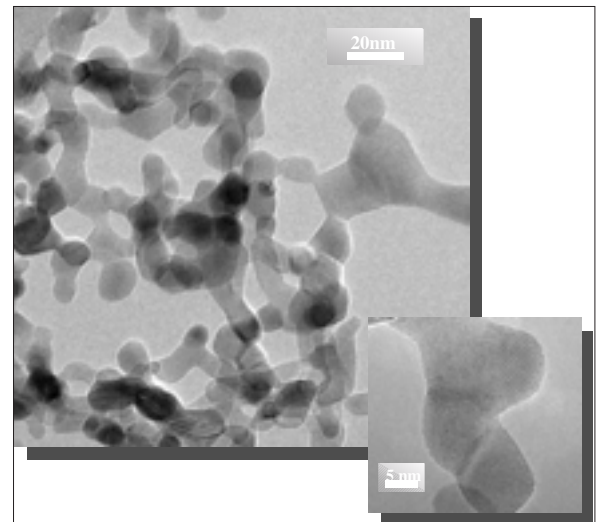


Fig. 1 TEM-micrograph of nanoscaled zirconia produced by Degussa AG

To prepare the conventional ZTA a microscaled 3 mol.%- Y_2O_3 -stabilized ZrO_2 (TZ 3Y-S, *Tosoh Corp*) was used. The product is finely ground and has an average particle size 0,4 μm and a specific BET surface of 7 m^2/g [9].

Specimens were produced by slip casting rather than pressing in order to simplify the tests. The slip was prepared by incorporating a surfactant, an organic binder and a defoaming agent (all supplied by *Zschimmer & Schwarz*).

Preparation of Specimens

Slip casting was used as a straightforward method to prepare the samples. Using the introduced raw materials, a slurry was prepared by using a laboratory ball mill. CT 3000SG, water and the deflocculant were milled for 3 hours with alumina balls (20 mm diameter) in a PE-milling pot. Subsequently the binder was added and the slurry was dispersed using an impeller mixer for additional 30 minutes. This slurry was called "A0". It served as basis for adding the ZrO_2 -raw materials and as a reference for an alumina ceramic.

By adding 12,6 mass % of the ZrO_2 -suspension VP Disp. W2650X to the alumina slurry, the ZrO_2 content was

| Raw material | A0 | n-ZTA | m-ZTA |
|-----------------|--|--|--------------------------|
| | Al ₂ O ₃ -basic-slurry | A0 + suspension of nanoscaled ZrO ₂ (VP Disp. W2650X) | A0 + microscaled TZ 3Y-S |
| addition: | | 5 Vol.% | 5 Vol.% |
| water | 23 mass % | | |
| deflocculant | 0,6 mass % | | |
| binder | 0,6 mass % | | |
| defoaming agent | 0,04 mass % | | |

Tab. 1 Formulation of A0, n-ZTA und m-ZTA

adjusted to 5 Vol.%. Dispersion was again done with an impeller mixer for 30 minutes. This slurry was called "n-ZTA" (Tab. 1).

The CT3000SG and the microscaled partially stabilized ZrO₂ (TZ3YS) are the raw materials for the slurry "m-ZTA". The addition of 5 Vol.% ZrO₂ to the CT3000SG was this time performed as the first step, because the microscaled ZrO₂ was used in granule form. The rest of the process was identical to the preparation of A0.

Samples were cast using plaster moulds measuring (6 x 8 x 60) mm. The mould and 3 samples are shown

| ramp [K/h] | temperature [°C] | hold time [h] |
|------------|------------------|---------------|
| 100 | 400 | |
| 300 | 1600 | 2 |
| 300 | RT | |

Tab. 2 Sintering program



Fig. 2 Casting of samples top: plaster mould, bottom: cast samples

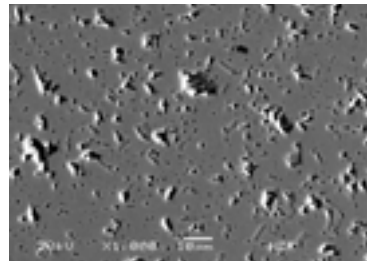


Fig. 3 Material A0

in Fig 2. Drying was performed at 110°C until the samples stopped losing mass. Sintering was done in a laboratory kiln according to the sintering program presented in Tab. 2.

Testing Methods

Measurement of the open porosity and bulk density was done according to EN 993-1 using a dipping and weighing method. 5 samples of each formulation were measured. For the determination of bending strength the 4-Point-Bending-Test according to DIN EN 843-1 was used. Again (3 x 4 x 50) mm samples were prepared, the undersides were polished and the edges were chamfered.

The assessment of the fracture toughness was performed by determining the K_{IC} -value. According to ENV 51109, the bending test of notched samples was used as testing method. Here again, samples with a measurement of (3 x 4 x 50) mm were used.

For SEM examination the sprue bush of a sample was embedded in epoxy-resin and polished to a 1 µm finish. These samples were also used for measuring the Vickers-hardness according to DIN 50733. After an initial SEM examination the samples were thermally etched. This causes grain boundary material to be

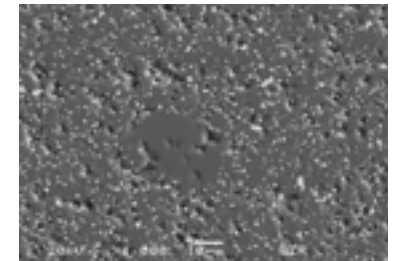
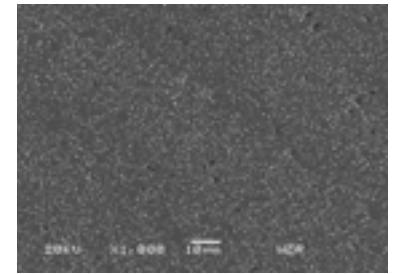


Fig. 4 (top) Material n-ZTA

Fig. 5 (bottom) Material m-ZTA

removed to reveal the grain structure of the sample. The microstructure of the treated samples appears in SEM examinations more three-dimensional.

Results

For all samples, porosity was found to be 0-Vol.%. It must be mentioned that only open pores were included in the porosity measurements. The SEM pictures clearly show visible pores, but these pores did not contact the water, because they are closed to the surface.

The density of the alumina ceramic is 3,99 g/cm³, and both ZTA-materials are about 4,05 g/cm³. This increase in density is due to the addition of zirconia in these samples.

The addition of microscaled zirconia leads to an increase in bending strength of approximately 100 MPa, an increase of 39 %, compared to the pure alumina ceramic. The addition of nanoscaled ZrO₂ in case of n-ZTA leads to an enhanced bending strength of 170MPa (+ 69 %).

A further effect of adding nanoscaled zirconia is that the fracture toughness rises: compared to 4,1 MPa·m^{1/2} for pure alumina, the K_{IC} -value of the n-ZTA increases by 15 %. The hardness of all samples is in the same range, between 18 and 19 GPa.

| | porosity [Vol.%] | | bulk density [g/cm ³] | | bending strength [MPa] | | K_{IC} [MPa · m ^{1/2}] | | hardness [GPa] | |
|-------|------------------|-------|-----------------------------------|-------|------------------------|-------|------------------------------------|-------|----------------|-------|
| | mean | σ (%) | mean | σ (%) | mean | σ (%) | mean | σ (%) | mean | σ (%) |
| A0 | 0 | 0 | 4,0 | 0,8 | 249 | 19,9 | 4,1 | 4,9 | 18,5 | 4,4 |
| n-ZTA | 0 | 0 | 4,1 | 0,5 | 420 | 9,5 | 4,7 | 4,2 | 18,7 | 2,9 |
| m-ZTA | 0 | 0 | 4,1 | 0,5 | 347 | 29,9 | 4,2 | 4,8 | 18,2 | 5,1 |

Tab. 3 Summary of physical data

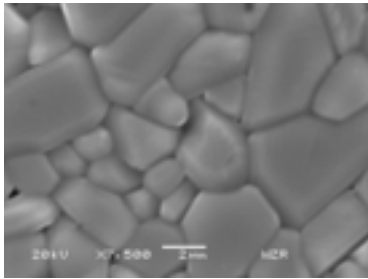


Fig. 6 Material A0 after thermal etching

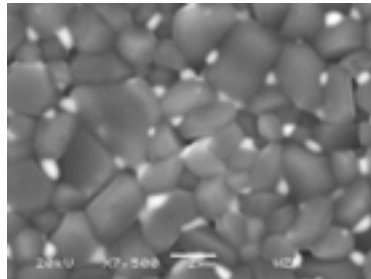


Fig. 7 Material n-ZTA after thermal etching

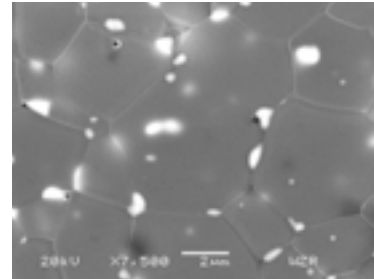


Fig. 8 Material m-ZTA after thermal etching

| | relative bulk density [%] | relative bending strenght [%] | relative K _{Ic} [%] | relative hardness [%] |
|-------|---------------------------|-------------------------------|------------------------------|-----------------------|
| A0 | 100 | 100 | 100 | 100 |
| n-ZTA | 102 | 169 | 115 | 101 |
| m-ZTA | 102 | 139 | 103 | 98 |

Tab. 4 Summary of physical data in relation to material A0

In general the n-ZTA material shows the lowest deviation of the measured values (see Tab. 3 for relative standard deviation σ in % of the mean value). Table 4 summarizes the physical data in relation to sample A0.

Figs. 3...5 show the polished sections of the materials A0, n-ZTA and m-ZTA. The microstructure of the 3 materials after thermal etching is shown in Figs. 6...8.

Discussion

The present study supports the results shown in [2,3] that indicate that addition of zirconia particles < 1 μ m leads to an increase in mechanical strength. The observations of Claussen [1] made with bigger particles that the addition of 5 Vol.% ZrO₂ will not lead to an increase in strength and fracture toughness, but to a slightly decreased hardness was not found with the examined materials n-ZTA and m-ZTA.

Comparing the materials n-ZTA and m-ZTA it is obvious that the particle size of the zirconia particles has a major impact on microstructure. By using zirconia particles in n-ZTA of about 100 nm, grain growth is significantly reduced (Figs. 6...8). The zirconia particles distribute homogeneously through the microstructure, fixing to the boundaries of the alumina grains and in this way limit their growth.

The n-ZTA material clearly shows enhanced bending strength and fracture toughness. The hardness remains as high as that of the pure alumina ceramic. All of these effects can be attributed to the homogeneity and fine size of the microstructure. In addition, the values of the bending strength of the n-ZTA show the smallest standard deviation of all three compared materials. This effect is well known in material sciences: standard deviation decreases with a finer microstructure since cracks and structure failures are smaller.

The study also indicates that in comparison to microscaled zirconia, a smaller amount of nanoscaled zirconia is necessary to improve the material properties of an alumina ceramic. In further investigations the effect of an amount below 5 Vol.% nanoscaled zirconia should be tested to determine whether a lower concentration such as 3 Vol.% would be effective in fixing the boundaries of the alumina grains.

Summary and Outlook

The preparation and testing of a pure alumina ceramic, an alumina ceramic with a 5 Vol.% nanoscaled zirconia (n-ZTA) addition and a ZTA-ceramic with 5 Vol.% microscaled ZrO₂ was performed in this work. The n-ZTA-material showed the best results. The addition of the nanoscaled ZrO₂ limits grain growth of the alumina resulting in increased

strength and fracture toughness. The deviation of the values is reduced and the material's hardness still remains on a high level.

Based of these findings, a ZTA-ceramic with nanoscaled ZrO₂ has considerable potential in applications with a high demand on strength, abrasion resistance and temperature or corrosion stability. Compared to a pure partially stabilized zirconia ceramic a better price-performance ratio and lower density of the n-ZTA-ceramic may be an advantage. The n-ZTA could find application in ceramic cutting tools or valve-, bearing- and pump-components (e.g. valve seats, tracks and rolling elements, rotors) and in the field of wear protection in mechanical and process engineering such as the linings of machines, tanks or conveyors.

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