

# Mechanical properties of $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated Y-TZP ceramics

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## Abstract

$\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated monoclinic  $\text{ZrO}_2$  nanopowder was prepared from a suspension of aluminiumnitrate, yttriumnitrate and  $\text{ZrO}_2$  powder in an alcohol/water mixture. The influence of the  $\text{Y}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  content as well as the sintering temperature on the mechanical properties of the densified yttria-stabilised tetragonal zirconia polycrystal (Y-TZP) materials was investigated. Fully dense Y-TZP materials could be obtained from the  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated starting powders by means of hot pressing in vacuum at 1450 °C. Typical  $\text{HV}_{10}$  hardness values of 1130 kg/mm<sup>2</sup> were obtained and the fracture toughness could be tailored up to 9 MPa m<sup>1/2</sup> by doping the 1.75–2.0 mol%  $\text{Y}_2\text{O}_3$ -coated  $\text{ZrO}_2$  starting powders with 2.0 wt.% of  $\text{Al}_2\text{O}_3$ . The properties and microstructures of the  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated powder based ceramics are compared with those of conventional co-precipitated 2Y and 3Y-TZP ceramics, and the differences in fracture toughness are explained in terms of the differences in the grain size and  $\text{Y}_2\text{O}_3$  distribution. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Coatings; Mechanical properties; Microstructure; Powders-chemical preparation; TZP;  $\text{ZrO}_2$

## 1. Introduction

Yttria-stabilised tetragonal zirconia polycrystalline ceramics (Y-TZP) are becoming popular engineering materials because of their excellent mechanical properties, especially their high fracture toughness. The fracture toughness is associated with the stress-induced transformation from tetragonal to monoclinic  $\text{ZrO}_2$ .<sup>1</sup> Stabilizers such as MgO, CaO,  $\text{Y}_2\text{O}_3$  and  $\text{CeO}_2$  are used to retain as much tetragonal phase as possible at room temperature after sintering. Yttria is the most commonly used stabiliser. The yttria content in Y-TZP ceramics plays an important role in the transformability of the tetragonal phase and therefore has a large influence on the toughness.

Most of the commercially available yttria-stabilised  $\text{ZrO}_2$  starting powders are synthesised by co-precipitation,<sup>2</sup> and the mechanical properties have been extensively studied during the past 20 years. In recent years

however, more attention is given to  $\text{Y}_2\text{O}_3$ -coated zirconia starting powders.<sup>3</sup> The bending strength and fracture toughness of densified Y-TZP ceramics obtained from yttria-coated zirconia starting powders are reported to be more attractive than those of ceramics based on co-precipitated powders, sintered under the same conditions.<sup>4</sup> It is also reported that yttria-coated and co-precipitated materials exhibit different fracture toughness trends with respect to the grain size dependence. Smaller grains of coated Y-TZP resulted in a high fracture toughness, whereas the opposite effect was observed in the co-precipitated materials, that show enhanced toughness with increasing grain size between a minimum grain size, needed to be transformable, and a maximum critical grain size, above which spontaneous transformation occurs.<sup>3</sup> An inhomogeneous stabiliser distribution, resulting in  $\text{ZrO}_2$  grains with a tetragonal shell around a monoclinic core, is suggested to be responsible for the excellent fracture toughness of yttria-coated  $\text{ZrO}_2$  powder based Y-TZP.<sup>3,4</sup>

The retention of the tetragonal  $\text{ZrO}_2$  phase after sintering is possible if the grain size of the dense polycrystalline materials is smaller than a critical size, which depends on the yttria content and the degree of mechanical constraint.<sup>1</sup> A grain boundary phase often plays an important role in the grain growth and sinterability and

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therefore can have a significant effect on the mechanical properties.

The addition of a small amount of alumina powder is reported to increase the fracture toughness of co-precipitated powder based Y-TZP ceramics.<sup>5</sup> The fracture toughness of sintered ceramics, obtained from mechanically mixed  $\text{Al}_2\text{O}_3$ /co-precipitated Y-TZP as well as powder from co-precipitated  $\text{Zr}^{4+}$ ,  $\text{Y}^{3+}$  and  $\text{Al}^{3+}$  mixtures, had an optimum fracture toughness at an alumina content of 5 vol.%.<sup>6</sup> Moreover, enhanced strength, fracture toughness and hardness were achieved by the addition of 10 vol.% alumina powder to co-precipitated 3 mol% Y-TZP materials.<sup>7</sup> No work however has been reported on the influence of small amounts of  $\text{Al}_2\text{O}_3$  in yttria-coated  $\text{ZrO}_2$  powder based ceramics.

In this paper, Y-TZP ceramics are prepared from  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated monoclinic  $\text{ZrO}_2$  nanopowder, formed from an alcohol/water suspension of aluminiumnitrate, yttriumnitrate and  $\text{ZrO}_2$  powder. The  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coating technique is a new alternative to the more conventional co-precipitation process. The work is focussed on the combined influence of the yttria and alumina content on the mechanical properties of densified  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated Y-TZP ceramics with yttria contents between 1.75 and 3.5 mol% and alumina contents between 0 and 5 wt.% which has not been reported before. The properties and microstructures are compared with those of conventional co-precipitated 2Y and 3Y-TZP ceramics and the superior fracture toughness of the  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated Y-TZP ceramics is explained in terms of the measured yttria distribution.

## 2. Experimental

The starting materials were yttrium nitrate hexahydrate ( $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Aldrich Chemical Company), aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Aldrich Chemical Company), and monoclinic zirconia nanopowder (Tosoh TZ-0) with a grain size between 50 and 100 nm. Stock suspensions with an yttrium and aluminium concentration of 0.1 M were used for the preparation of the  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated  $\text{ZrO}_2$  nanopowders. To break the agglomerates in the  $\text{ZrO}_2$  starting powder, Y-TZP milling balls (Tosoh TZ-3Y) were added to the suspension. In order to avoid additional contamination, mixing was performed in polyethylene containers. The water/propanol ratio was 1. After drying of the suspension with a rotating evaporator, the powder was calcined in air at 450–800 °C. More information on the powder coating procedure is given elsewhere.<sup>8</sup>

Densification was performed by means of hot pressing since the final goal is to develop  $\text{ZrO}_2$ -based composites containing non-oxide secondary phase up to 50 vol.%. The dried powder was inserted into a cylindrical graphite die with a diameter of 30 mm, coated with boron

nitride. After cold compression at 20 MPa, the samples were hot pressed in a KCE hot press (W 100/150-2200-50 LAX, KCE Sondermaschinen, Rödental, Germany) in vacuum ( $\approx 0.1$  Pa), during 1 h under a mechanical load of 20 MPa. Hot press temperatures used were 1400, 1450 or 1500 °C with a heating rate of 50 °C/min, a dwell time of 1 h and a cooling rate of 10 °C/min.

The crystalline phases of the powders, polished samples and fracture surfaces were determined by X-ray diffractometry (XRD, Philips, The Netherlands), whereas the microstructure of thermally etched (20 min in air at 1400 °C) cross-sections was investigated by scanning electron microscopy (SEM, Philips XL-30-FEG). Grain size distributions were obtained from the linear intercepts of 200 grains measured on the thermally etched surfaces. The grain size data are presented as measured since no mathematical corrections were performed. The measurement system of the SEM was calibrated with a calibrating grid.

The Vickers hardness ( $\text{HV}_{10}$ ) was measured on a Zwick hardness tester with a load of 10 kg. The  $K_{\text{IC}}$  was measured by the Vickers  $\text{HV}_{10}$  indentation technique. The  $K_{\text{IC}}$  values were calculated according to the formula of Anstis et al.<sup>9</sup> The elastic modulus,  $E$ , of the ceramic specimen was measured by the resonance frequency method using a Grindo-Sonic according to ASTM C 1259-94. The density of the specimen was measured in ethanol, according to the Archimedes method (BP210S balance, Sartorius AG, Germany).

## 3. Results and discussion

### 3.1. $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated powder based Y-TZP

In order to study the influence of the sinter temperature on the mechanical properties, a 2.0 wt.%  $\text{Al}_2\text{O}_3/2.5$  mol%  $\text{Y}_2\text{O}_3$  coated  $\text{ZrO}_2$  powder was hot pressed for 1 h at 1400, 1450 and 1500 °C. The mechanical properties obtained are presented in Table 1. From these data, it is clear that the powder can be fully densified at all investigated temperatures. The hardness decreases with increasing hot pressing temperature, whereas the fracture toughness is maximum when hot pressing at 1450 °C. SEM micrographs of the starting powder and polished and thermally etched (20 min in air at 1400 °C) cross-sections of the same materials are shown in Fig. 1.

The grain size of the starting powder is between 50 and 100 nm, as shown in Fig. 1a. The grain size of the Y-TZP materials clearly increases with increasing sintering temperature. The grain size is small ( $< 0.5$   $\mu\text{m}$ ) for the specimen sintered at 1400 °C. At 1450 and 1500 °C, the microstructure becomes coarser and bimodal (see Fig. 1c). The microstructure consists of large cubic zirconia (c- $\text{ZrO}_2$ ) grains in a much finer tetragonal zirconia (t- $\text{ZrO}_2$ ) matrix. The increasing grain size correlates with a decreasing hardness, as shown in Table 1. Submicron

Table 1  
Mechanical properties of 2 wt.%  $\text{Al}_2\text{O}_3$ /2.5 mol%  $\text{Y}_2\text{O}_3$ -coated Y-TZP ceramics as a function of the hot pressing temperature

Hot press temperature ( $^{\circ}\text{C}$ )	$K_{\text{IC}}$ ( $\text{MPa m}^{1/2}$ )	$\text{HV}_{10}$ ( $\text{kg/mm}^2$ )	Density ( $\text{g/cm}^3$ )
1400	$5.2 \pm 0.8$	$1274 \pm 18$	6.02
1450	$6.2 \pm 0.5$	$1199 \pm 16$	6.02
1500	$4.6 \pm 0.5$	$1188 \pm 13$	6.02

alumina grains (dark on the micrographs) can be distinguished in the zirconia matrix. This clearly indicates that well-defined alumina crystals are formed in-situ from the molecularly dispersed  $\text{Al}_2\text{O}_3$  precursor during sintering.

XRD analysis revealed the complete conversion of the monoclinic coated  $\text{ZrO}_2$  starting powder into tetragonal and cubic  $\text{ZrO}_2$  after sintering at  $1450^{\circ}\text{C}$ , as shown in Fig. 2.

### 3.2. $\text{Al}_2\text{O}_3$ -addition

The influence of the alumina content on the mechanical properties of yttria-coated TZP ceramics was investigated by hot pressing 2.5 mol% yttria-coated  $\text{ZrO}_2$

powder with varying alumina content for 1 h at  $1450^{\circ}\text{C}$ . The mechanical properties are summarised in Table 2 and the hardness and fracture toughness are graphically presented in Fig. 3.

The yttria-coated sample without alumina addition spontaneously transformed to m- $\text{ZrO}_2$ . Therefore, no mechanical properties are reported. XRD analysis of polished surfaces of the samples containing 1–4 wt.%  $\text{Al}_2\text{O}_3$  revealed the absence of m- $\text{ZrO}_2$ . The m- $\text{ZrO}_2$  content measured on fractured surfaces on the other hand was high, indicating a very active transformation toughening mechanism. The measured m- $\text{ZrO}_2$  contents are reported in Table 2.

The density linearly decreases with increasing alumina content, due to the lower density of  $\text{Al}_2\text{O}_3$ , i.e.  $3.89 \text{ g/cm}^3$ . Optical microscopical observation of polished cross-sections revealed no porosity. The  $E$ -modulus and hardness are approximately constant with increasing alumina content up to 5 wt.%. The fracture toughness however clearly shows a maximum at an alumina content of 2 wt.% (3 vol.%). No direct correlation however is found between the fracture toughness and the amount of m- $\text{ZrO}_2$  measured on fracture surfaces (see Table 2). The optimum fracture toughness of the yttria/alumina-coated

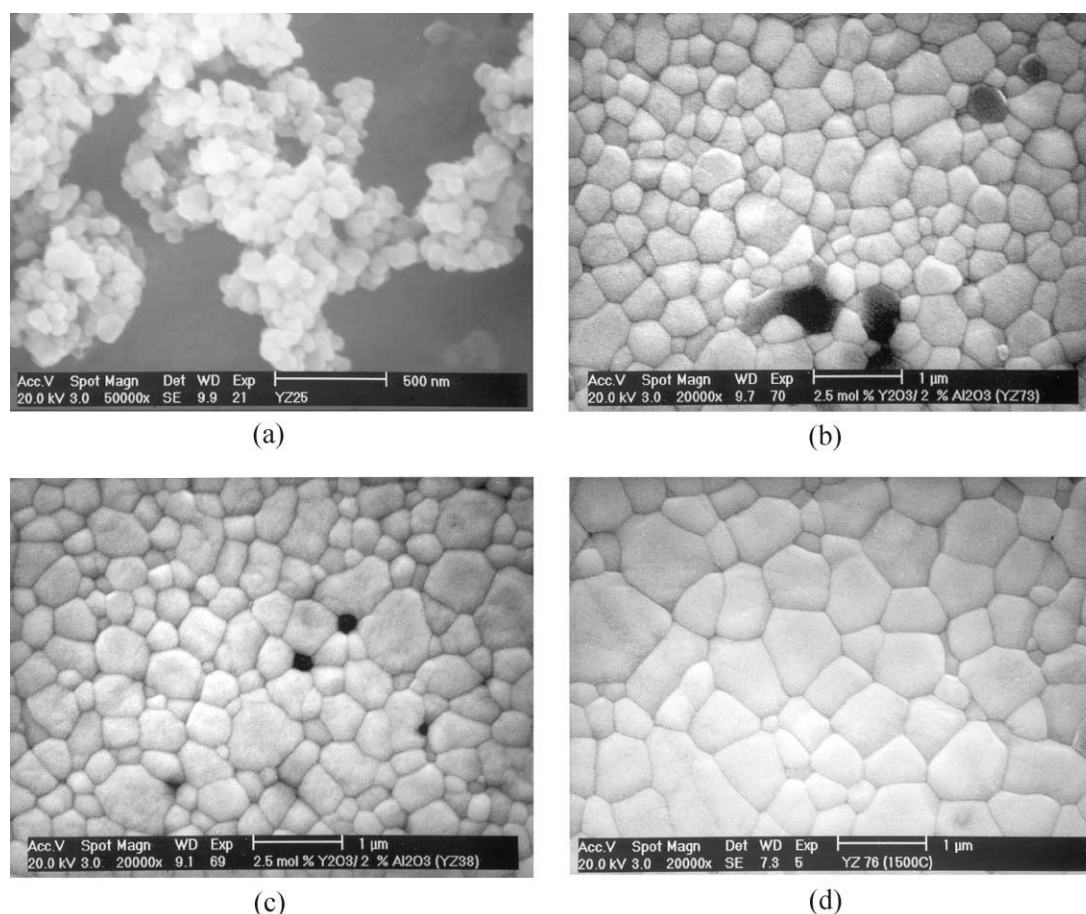


Fig. 1. Micrographs of materials prepared from a 2.0 wt.%  $\text{Al}_2\text{O}_3$ /2.5 mol%  $\text{Y}_2\text{O}_3$  coated  $\text{ZrO}_2$  powder: starting powder (a) and thermally etched Y-TZP ceramics, hot pressed at  $1400^{\circ}\text{C}$  (b),  $1450^{\circ}\text{C}$  (c) and  $1500^{\circ}\text{C}$  (d).

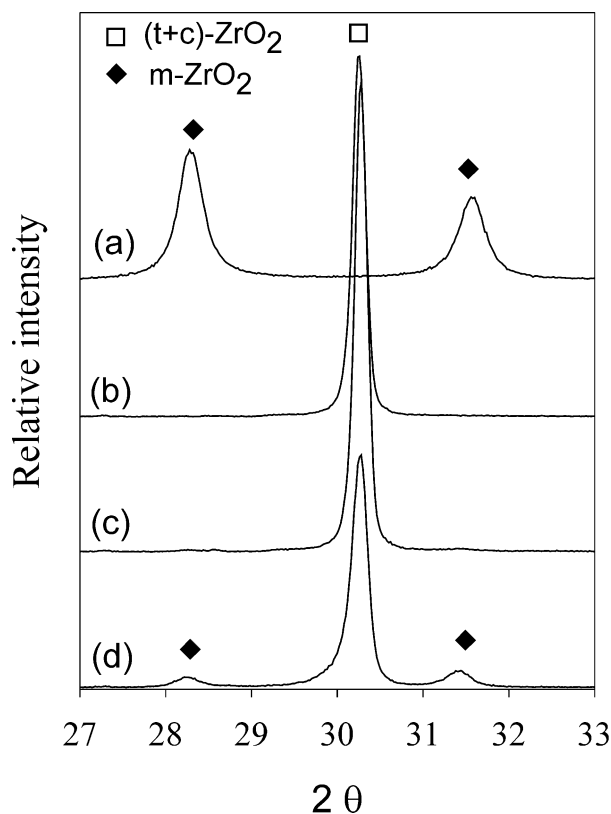


Fig. 2. Diffraction patterns of the dried 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated  $\text{ZrO}_2$  starting powder (a) and polished 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated powder based ceramics with 3.0 (b), 2.5 (c) and 2.0 (d) mol%  $\text{Y}_2\text{O}_3$ , hot pressed during 1 h at 1450 °C.

powder based ceramics at low alumina contents is in agreement with the observations reported for co-precipitated  $\text{ZrO}_2$  powder based ceramics.<sup>7</sup> It has been reported that a relatively small amount of alumina (5–10 vol.%) can be added to yttria co-precipitated  $\text{ZrO}_2$  powders to make Y-TZP ceramics with strength, toughness and hardness characteristics that are higher than those exhibited by the pure zirconia matrix.<sup>5–7,10</sup> This effect in co-precipitated  $\text{ZrO}_2$  powder based materials has been attributed to the grain growth retarding effect of the alumina addition.<sup>11</sup> The grain growth retarding effect of alumina in Y-TZP, obtained from Al-Y-co-precipitated<sup>13</sup> as well as Y-co-precipitated powder

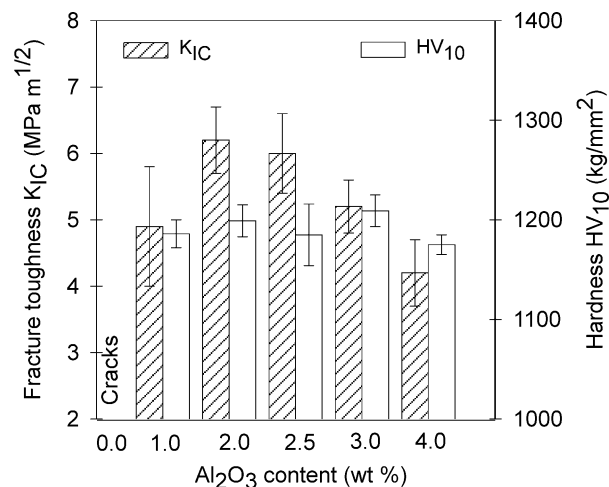


Fig. 3. Hardness and fracture toughness of 2.5 mol%  $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ -coated Y-TZP ceramics as a function of the alumina content.

with  $\text{Al}_2\text{O}_3$  powder added,<sup>12</sup> is probably led by the grain boundary pinning effect<sup>12</sup> and in the case of Al-Y-co-precipitated powder also by the reduction of the crystallization rate. The grain growth inhibiting effect of the addition of alumina particles to co-precipitated powder based Y-TZP ceramics was clearly illustrated to increase with decreasing alumina particle size.<sup>14</sup> In another study however, the grain size of the tetragonal  $\text{ZrO}_2$  phase was reported to be independent of the addition of up to 12 wt.% of  $\text{Al}_2\text{O}_3$ ,<sup>15</sup> whereas the low-temperature degradation during annealing in water was remarkably suppressed.<sup>15,16</sup> In another report, the optimum fracture toughness obtained when adding 10 vol.% of alumina particles to co-precipitated  $\text{ZrO}_2$  powder could be correlated with an enhanced tetragonal to monoclinic phase transformation observed on fracture surfaces.<sup>7</sup> A similar increase in fracture toughness was reported for 2 and 2.5 mol%  $\text{Y}_2\text{O}_3$  co-precipitated powder based Y-TZP materials with  $\text{Al}_2\text{O}_3$  additions up to 2 wt.%.<sup>5</sup> The increase in fracture toughness was found to correlate well with an increased transformation zone size.<sup>5</sup> The residual tensile stress in zirconia however showed no clear correlation with the volume fraction of added alumina particles, and was found to increase with increasing zirconia grain size.<sup>14</sup>

Table 2

Mechanical properties of 2.5 mol%  $\text{Y}_2\text{O}_3$ -coated Y-TZP ceramics as a function of the  $\text{Al}_2\text{O}_3$  content, hot pressed for 1 h at 1450 °C

Alumina content (wt. %)	$K_{IC}$ (MPa m <sup>1/2</sup> )	HV <sub>10</sub> (kg/mm <sup>2</sup> )	E (GPa)	Density (g/cm <sup>3</sup> )	m-ZrO <sub>2</sub> <sup>a</sup> (%)
1.00	4.6±0.8	1186±14	212	6.04	26.1
2.00	6.2±0.5	1199±16	215	6.02	24.1
2.50	5.7±0.5	1185±31	229	5.98	21.9
3.00	5.2±0.4	1209±16	209	5.95	25.2
4.00	3.7±0.4	1175±10	221	5.91	24.8

<sup>a</sup> Overall monoclinic- $\text{ZrO}_2$  phase content (percentage of total zirconia) measured on fracture surfaces.

It can be concluded from the above that the fracture toughness of yttria-coated powder based TZP ceramics can be optimized by the addition of a small amount of  $\text{Al}_2\text{O}_3$ , similar to co-precipitated powder based TZP materials. The exact mechanism however remains unclear.

### 3.3. $\text{Y}_2\text{O}_3$ content

The influence of the overall yttria content on the mechanical properties was studied by hot pressing yttria/alumina-coated powders with 2 wt.%  $\text{Al}_2\text{O}_3$  and a varying yttria content. The mechanical properties are summarized in Table 3 and the fracture toughness and hardness of the ceramics are graphically presented in Fig. 4.

Full density was obtained for all investigated specimens, except for the 1.5 mol% yttria-coated TZP. The latter sample suffered from spontaneous transformation of tetragonal to monoclinic  $\text{ZrO}_2$ , resulting in the formation of micro- and macrocracks which also reduced the hardness.

The hardness slightly increased with increasing yttria content at a constant alumina level, whereas

the  $E$ -modulus is hardly influenced by the yttria and alumina content. The toughness strongly decreases with increasing yttria content at constant alumina level. Below an overall yttria content of 1.75 mol%, spontaneous transformation of tetragonal  $\text{ZrO}_2$  was observed. The fracture toughness can be tailored from 3.9 up to 9.3  $\text{MPa m}^{1/2}$  by reducing the yttria content from 3.5 to 1.75 mol% at the 2 wt.% alumina level.

The decrease in fracture toughness with increasing yttria content in the hot pressed alumina/ytria-coated ceramics is similar to the data reported for Y-TZP ceramics obtained from co-precipitated powders, and has to be correlated with a decreasing grain size and transformability with increasing yttria content.<sup>17</sup> The slightly increasing hardness with increasing yttria content clearly reflects the decreasing grain size. Microstructural evidence for the decreasing grain size with increasing yttria content is given in Fig. 5.

### 3.4. Coated and co-precipitated Y-TZP

The microstructures of the 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated Y-TZP ceramics with 2 and 3 mol%  $\text{Y}_2\text{O}_3$  are compared with those of 2 and 3 mol% yttria stabilised co-precipitated Y-TZP materials obtained under exactly the same hot pressing conditions in Fig. 5. The mechanical properties are compared in Table 4, the grain size distributions are presented in Fig. 6 and the yttria-distribution profiles, as obtained by EPMA point analysis, of the 3Y-TZP materials are compared in Fig. 7.

The average grain size of the co-precipitated 2Y-TZP ceramic is 390 nm, which is higher than that of the co-precipitated 3Y-TZP, being 321 nm. The average grain size of the alumina/ytria-coated powder based ceramics are higher than that of the corresponding co-precipitated ceramics. The average grain size of the 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated 2Y-TZP and 3Y-TZP ceramic is 429 and 408 nm, respectively. The grain size of the co-precipitated as well as yttria-coated powder based materials decreases with increasing yttria content.

The grain size distribution of the yttria-coated powder based Y-TZP ceramics is broader than that of the co-precipitated powder based materials, as shown in Fig. 6. The microstructures of the yttria-coated powder based materials reveal the presence of a certain amount of larger grains, which are not present in the co-precipitated  $\text{ZrO}_2$  powder based ceramics. From their high yttria content it can be deduced that these larger grains are actually cubic  $\text{ZrO}_2$  grains. The presence of larger cubic grains is characteristic for yttria-coated powder based Y-TZP ceramics, even for those with a relatively low yttria content (down to 2 mol%) sintered at temperatures as low as 1450 °C.<sup>3</sup> In the grain size distributions, the cubic grains correspond to the fraction of grains having a grain size above 0.8  $\mu\text{m}$ .

Table 3  
Mechanical properties of 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated Y-TZP ceramics as a function of the yttria content, hot pressed for 1 h at 1450 °C

Yttria content (mol%)	$K_{\text{IC}}$ ( $\text{MPa m}^{1/2}$ )	$\text{HV}_{10}$ ( $\text{kg/mm}^2$ )	$E$ (GPa)	Density ( $\text{g/cm}^3$ )
1.50	$4.4 \pm 0.2$	$956 \pm 15$	224	5.72
1.75	$9.3 \pm 0.7$	$1137 \pm 9$	208	6.04
2.00	$8.5 \pm 1.1$	$1120 \pm 13$	211	5.99
2.25	$5.3 \pm 0.7$	$1176 \pm 9$	204	6.04
2.50	$6.1 \pm 0.5$	$1199 \pm 16$	215	6.02
2.62	$4.6 \pm 0.3$	$1223 \pm 8$	215	6.02
2.75	$4.2 \pm 0.2$	$1214 \pm 29$	222	6.02
3.00	$5.1 \pm 0.7$	$1207 \pm 16$	211	6.01
3.50	$3.9 \pm 0.3$	$1264 \pm 16$	202	5.97

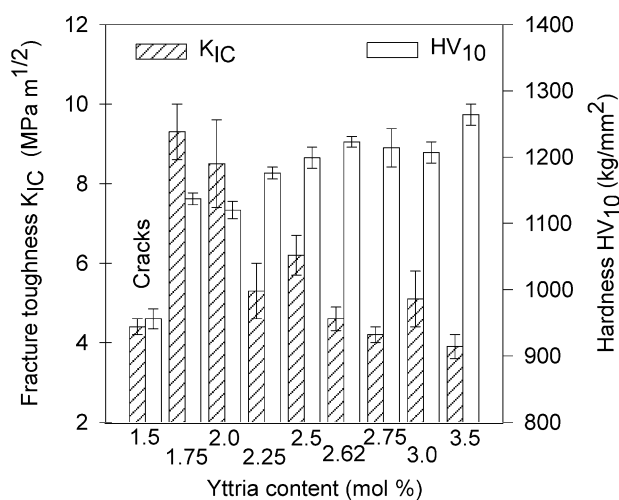


Fig. 4. Hardness and fracture toughness of 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated Y-TZP ceramics as a function of the yttria content.

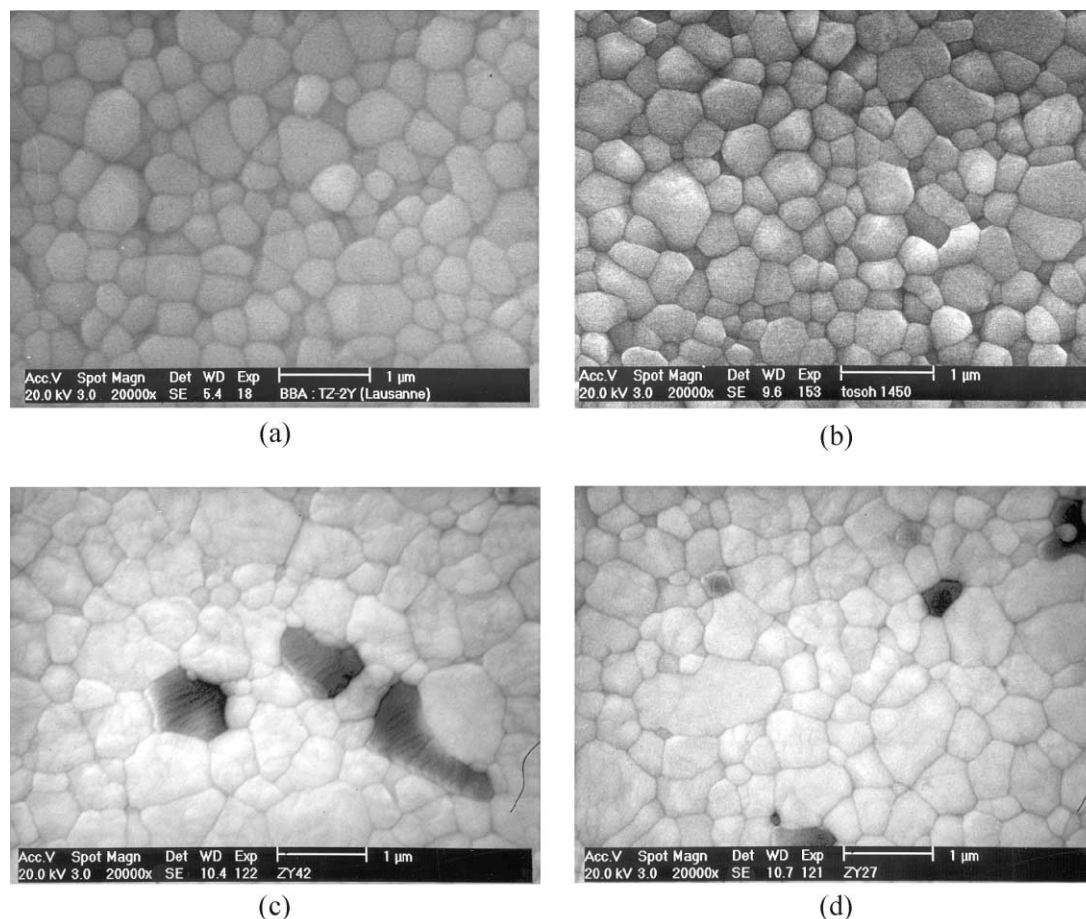


Fig. 5. Thermally etched microstructures of co-precipitated 2Y-TZP (a) and 3Y-TZP (b) compared with 2 wt.% Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>-coated 2Y-TZP (c) and 3Y-TZP (d) ceramics. The dark grains are Al<sub>2</sub>O<sub>3</sub> particles.

Table 4

Mechanical properties of the sintered Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>-coated TZP, and ceramics obtained from commercially available co-precipitated powders, hot pressed in vacuum at 1450 °C

	Alumina content (wt.%)	Yttria content (mol%)	$K_{IC}$ (MPa m <sup>1/2</sup> )	HV <sub>10</sub> (kg/mm <sup>2</sup> )	$E$ (GPa)	Density (g/cm <sup>3</sup> )
Y <sub>2</sub> O <sub>3</sub> -coated	2.00	2.00	8.5±1.1	1120±13	211	5.99
Y <sub>2</sub> O <sub>3</sub> -coated	2.00	3.00	5.1±0.7	1207±16	211	6.01
Tosoh (TZ-2Y)	< 0.005	2.00	5.9±0.1	1086±42	Cracks	6.06
Tosoh (TZ-3Y)	< 0.005	3.00	2.5±0.1	1188±16	194	6.08
Tosoh (TZ-3Y-E)	0.25	3.00	4.1±0.2	1260±22	212	6.06
Tosoh (TZ-3Y)	2.00 (SM8)	3.00	3.3±0.1	1225±18	200	5.98

The yttria-distribution profile of the yttria-coated powder based 3Y-TZP ceramic is much broader than that of the co-precipitated 3Y-TZP, as shown in Fig. 7. The high yttria levels (> 8 mol% yttria) measured in the yttria-coated powder based ceramic correspond with cubic ZrO<sub>2</sub> grains, mentioned above.

The narrow yttria distribution in the co-precipitated powder based ceramics results in a relatively narrow tetragonal grain size distribution, whereas the broader yttria distribution of the Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>-coated powder

based ceramics results in a broader tetragonal grain size distribution with additional cubic ZrO<sub>2</sub> grains. The correlation between the yttria and tetragonal ZrO<sub>2</sub> grain size distribution curves for both material grades on the one hand and the stability or transformability of the ZrO<sub>2</sub> material on the other hand is schematically presented in Fig. 8. It can be deduced from this figure that the transformability as well as the fracture toughness of the yttria-coated ceramics will be higher than that of the co-precipitated powder based TZPs, due to the additional

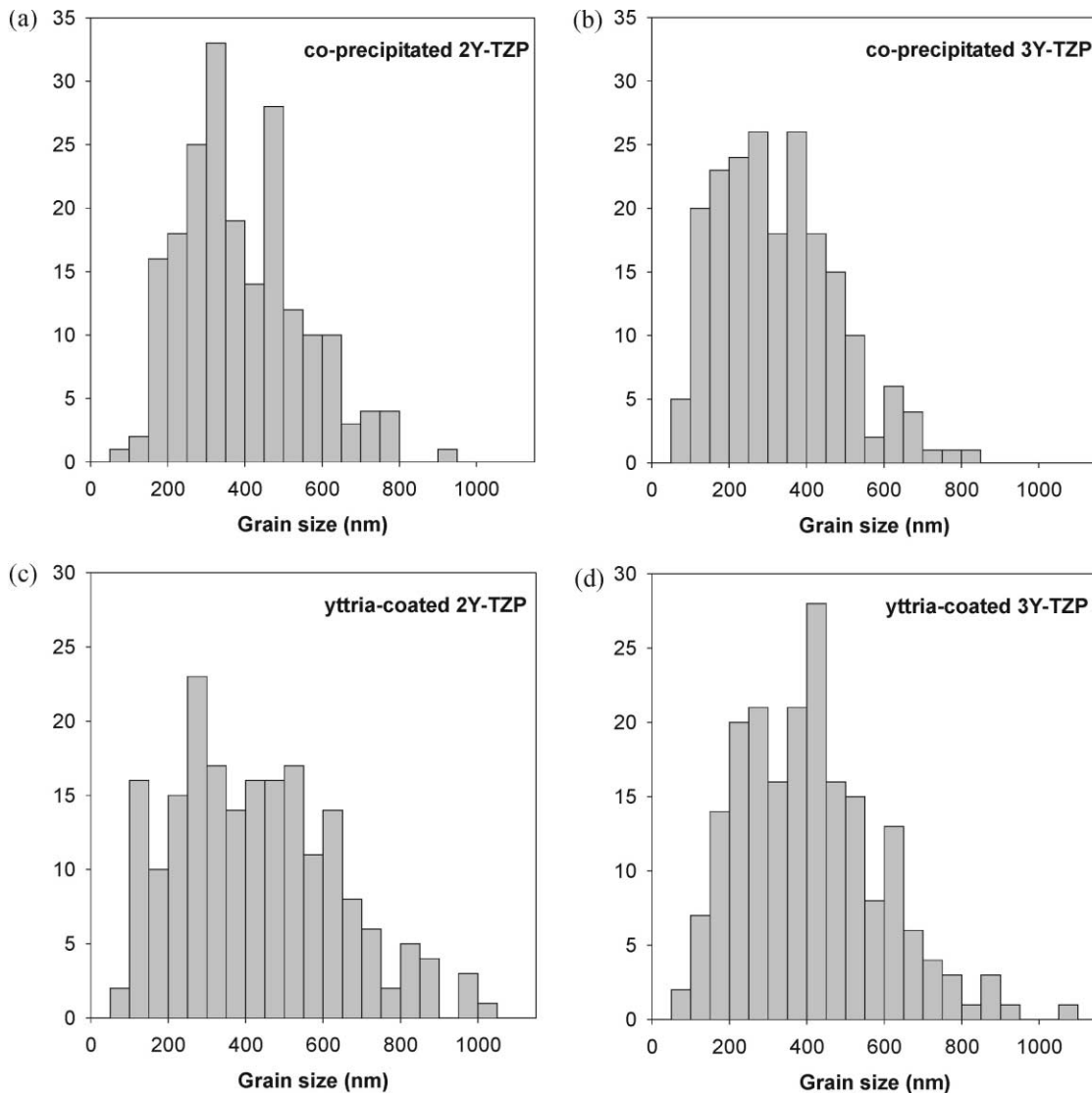


Fig. 6.  $\text{ZrO}_2$  grain size distributions of co-precipitated 2Y-TZP (a) and 3Y-TZP (b) compared with 2 wt.%  $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ -coated 2Y-TZP (c) and 3Y-TZP (d) ceramics.

fraction of tetragonal  $\text{ZrO}_2$  grains with a low yttria content and a larger grain size. It should be noted here that the size of the fraction of grains with an yttria content below 1 mol% is expected to be somewhat in-between that of the small tetragonal grains and the cubic grains.<sup>18</sup>

The data given in Table 4 reveals that the fracture toughness of the coated 2Y-TZP and 3Y-TZP ceramics with 2 wt.%  $\text{Al}_2\text{O}_3$  is superior to that of the co-precipitated 2Y-TZP and 3Y-TZP materials without  $\text{Al}_2\text{O}_3$ . Additional experiments revealed that the fracture toughness of the co-precipitated 3Y-TZP material can be increased by the addition of 2 wt.% of submicron  $\text{Al}_2\text{O}_3$  powder (Baikowski grade SM8) or the use of the special Tosoh grade (TZ-3Y-E) with 0.25 wt.% of  $\text{Al}_2\text{O}_3$  (see Table 4).

The highest fracture toughness was obtained for the 2 wt.%  $\text{Al}_2\text{O}_3$ /yttria-coated 2Y-TZP, whereas the material

obtained from the co-precipitated 2Y-TZP powder was susceptible to spontaneous transformation, resulting in macrocracking and a low hardness. Despite the presence of about 12% of m- $\text{ZrO}_2$  on the polished 2 wt.%  $\text{Al}_2\text{O}_3$ /yttria-coated 2Y-TZP, as revealed by XRD investigation (see Fig. 2d), no cracks were observed in the sample. The presence of m- $\text{ZrO}_2$  might also be partially or completely induced by polishing, due to the high transformability of the sample. No m- $\text{ZrO}_2$  was observed on the 2 wt.%  $\text{Al}_2\text{O}_3$ /yttria-coated 3Y-TZP, as shown in Fig. 2b.

Sintering of yttria-coated powder is reported to result in  $\text{ZrO}_2$  grains with an yttria-rich shell and a core with low yttria content, due to the low diffusion rate of yttria.<sup>19</sup> In the extreme case, a tetragonal shell can be formed around a monoclinic core.<sup>3,19</sup> It has been suggested that the enhanced transformability of the core structure is responsible for the high fracture toughness

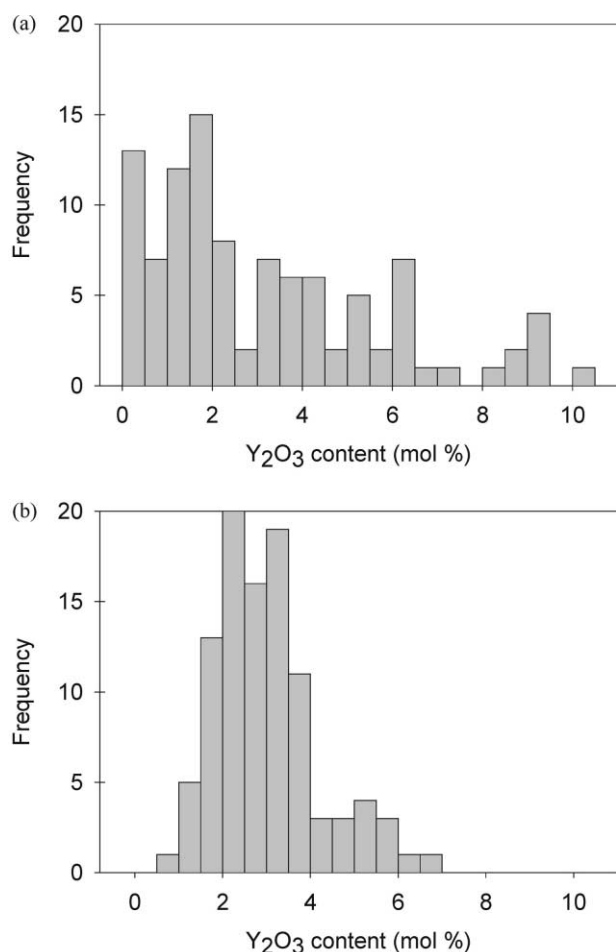


Fig. 7. Yttria distribution profiles of a 2 wt.% Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>-coated (a) and a co-precipitated (b) 3Y-TZP ceramic.

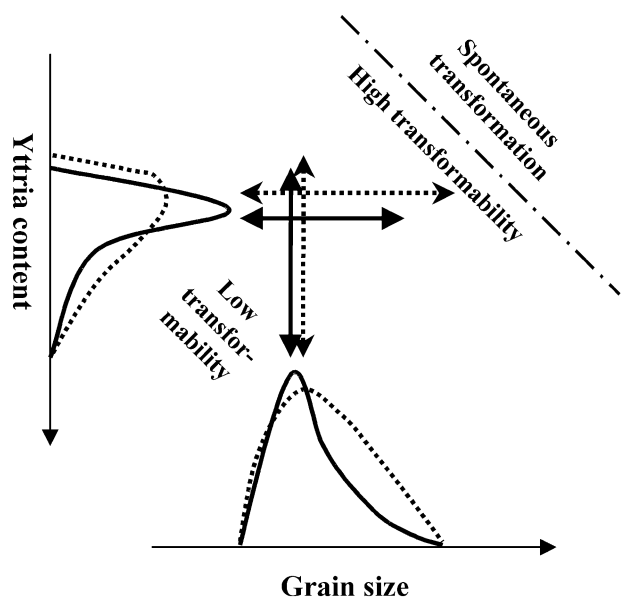


Fig. 8. Schematic presentation of the yttria and grain size distribution in yttria-coated (dashed line) and yttria co-precipitated (full line) ZrO<sub>2</sub> powder based Y-TZP.

of coated Y-TZP.<sup>3</sup> In the case of co-precipitated powder based Y-TZP, a strong yttrium segregation to the grain boundaries is reported in several Y-TZP materials, despite different grain sizes and impurity levels. The results showed that the segregation however was confined to an area of less than 5 nm around the grain boundary plane.<sup>20–22</sup>

TEM investigation did not indicate the presence of core-shell grains in the yttria-coated powder based ceramics. The higher fracture toughness of the yttria-coated powder based ceramics therefore has to be related to the inhomogeneous yttria distribution and broader grain size distribution in these ceramics. The yttria content in the coated TZP is partly concentrated in the non-transformable large cubic grains, which contain a relatively high amount of yttria (>8 mol%) and do not contribute to transformation toughening. The low yttria content grains, which are not present in co-precipitated powder based Y-TZP, are mainly tetragonal and should be extremely sensitive to transformation. These highly transformable grains will therefore act as primary nucleation sites for transformation under an applied external stress.

A similar inhomogeneous yttria distribution, without the formation of cubic grains, can be achieved by mixing of co-precipitated and monoclinic ZrO<sub>2</sub> starting powders. The toughness enhancement that can be achieved by powder mixing<sup>23</sup> is comparable to that of the yttria-coating technique.

From the information presented above, it is clear that yttria-coated ZrO<sub>2</sub> starting powders result in Y-TZP ceramics containing large c-ZrO<sub>2</sub> grains and a fraction of highly transformable t-ZrO<sub>2</sub> grains with low yttria content and larger grain size, whereas co-precipitated powders result in a fully t-ZrO<sub>2</sub> material with a narrow yttria distribution and a grain size distribution with a larger fraction of smaller grains, having an overall lower susceptibility to transformation.

#### 4. Conclusions

Fully dense Y-TZP ceramics can be obtained by hot pressing of Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>-coated monoclinic ZrO<sub>2</sub> nanopowders, prepared from a suspension of aluminium-nitrate, yttrium-nitrate and ZrO<sub>2</sub> powder in an alcohol/water mixture.

The fracture toughness of Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>-coated powder based TZP ceramics can be tailored by selection of the overall Y<sub>2</sub>O<sub>3</sub> content. A maximum toughness for Y-TZP with 2 wt.% alumina was obtained with an yttria content of 1.75 mol%. The optimum toughness of Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>-coated based Y-TZP was achieved at a hot pressing temperature of 1450 °C. The fracture toughness of the yttria-coated powder based TZP ceramics could be optimised by the addition of 2 wt.% Al<sub>2</sub>O<sub>3</sub>.



Yttria-coated  $\text{ZrO}_2$  starting powders result in Y-TZP ceramics with a broad yttria and grain size distribution, containing large c- $\text{ZrO}_2$  grains and a fraction of highly transformable t- $\text{ZrO}_2$  grains with low yttria content, whereas co-precipitated powders result in a fully t- $\text{ZrO}_2$  material with a narrow yttria and grain size distribution, having a lower transformability. The superior toughness of the yttria-coated powder based ceramics is due to the presence of a fraction of larger tetragonal  $\text{ZrO}_2$  grains with low yttria content.

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