Journal of the European Ceramic Society **11** (1993) 497–507

The Preparation and Characterization of Y-TZP/20 wt% Alumina

P. den Exter, A. J. A. Winnubst* & A. J. Burggraaf

University of Twente, Faculty of Chemical Technology, Laboratory of Inorganic Chemistry, Materials Science and Catalysis, PO Box 217, 7500 AE Enschede, The Netherlands

(Received 3 June 1992; accepted 10 July 1992)

Abstract

Zirconia (+2–2·5 mol% yttria)/12–20 wt% alumina composite powders have been prepared by several techniques. The preparation methods were discussed in terms of powder characteristics, densification behaviour and microstructure. The densification behaviour of the composites depended on the crystal structure of the phases and on the dispersion of the alumina in the Y-TZP matrix. Both the spraying and coprecipitation methods resulted in an inhomogeneous dispersion and a relatively low density (95%), caused by either differential sintering of alumina aggregates (coprecipitation method) or by an inhomogeneous dispersion of the alumina (spraying method). Both the acetyl acetonate and the α-alumina methods resulted in high density (98%) ceramics in which the alumina was homogeneously dispersed. The α-alumina method, however, required higher sintering temperatures (1450°C) than the acetyl acetonate method. Both methods gave better results than those obtained with a commercially available powder.

Verbunde aus Zirkoniumdioxid mit 2–2·5 Mol% Yttriumzusatz und zu 12–20 Gew.% aus Aluminiumoxid wurden mit Hilfe verschiedener Techniken hergestellt. Die Herstellungsmethoden wurden in Hinblick auf die Pulvereigenschaften, das Verdichtungsverhalten und das Gefüge besprochen. Das Verdichtungsverhalten der Verbunde hängt von der Kristallstruktur der beteiligten Phasen und von der Verteilung des Aluminiumoxids in der Y-TZP-Matrix ab. Sowohl die Sprüh- als auch die Koausscheidungsmethode ergaben eine inhomogene Verteilung und eine relativ geringe Dichte (95%). Dieses ist entweder auf differentielles Sinterverhalten der Alumiumdioxid-Aggregate (Koausscheidungsmethode) oder auf eine inhomogene Verteilung der Aluminiumoxid-Teilchen (Sprühmethode) zurückzuführen. Im Gegensatz hierzu ergaben die Acetyl-Acetonat- und die α-Aluminiumoxid-Methode Keramiken mit hoher Dichte, in denen die Aluminiumoxid-Phase homogen verteilt war. Die α-Aluminiumoxid-Methode erforderte höhere Sintertemperaturen (1450°C) als die Acetyl-Acetonat-Methode. Beide Verfahren führten zu besseren Ergebnissen als mit der Anwendung handelsüblicher Pulver erzielt werden konnten.

Des poudres composites en zircone (+2–2·5 mol% d'Y_2O_3)/12–20 wt% alumine ont été préparées par diverses techniques. Les méthodes de préparation sont discutées en termes de caractéristiques des poudres, de comportement à la densification et de microstructure. La densification des composites dépend de la structure cristalline et de la dispersion de l'alumine dans la matrice en Y-TZP. Aussi bien la méthode par pulvérisation que celle par coprécipitation résultent en une dispersion hétérogène et en une densification relativement faible (95%), provenant d'un frittage différentiel des agrégats d'alumine (méthode par coprécipitation) ou d'une dispersion hétérogène de l'alumine (méthode par pulvérisation). Les méthodes acétyl-acétonate et alumine-α permettent d'atteindre des densités élevées (98%) et d'obtenir une dispersion homogène de l'alumine. La méthode alumine-α requiert cependant une température de frittage plus élevée (1450°C) que la méthode acétyl-acétonate. Les deux méthodes conduisent à des résultats meilleurs que ceux obtenus à partir d'une poudre commerciale.

1 Introduction

The high strength and fracture toughness of yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) is due to the phase transformation from tetragonal zirconia to the monoclinic structure during mechanical loading. For brittle composite materials con-

* To whom correspondence should be addressed.

Journal of the European Ceramic Society 0955-2219/93/$6.00

taining Y-TZP Lange[1] derived an equation for the increase in fracture toughness due to the stress-induced phase transformation:

$$K_c = \sqrt{K_o^2 + \frac{2RV_i E_c(|\Delta G_c| - \Delta U_{se} f)}{(1 - \nu_c^2)}} \quad (1)$$

where K_c is the critical stress intensity factor, K_o the critical stress intensity for the material without transformation phenomenon, $|\Delta G_c|$ is the change in chemical free energy associated with the transformation, ΔU_{se} is the change in strain energy associated with the transformation, $(1-f)$ is the loss of strain energy due to the loss of constraint imposed on the dispersed particles during crack extension, V_i the volume fraction of transformed particles, ν_c the Poisson's ratio, E_c the Young's modulus of the composite and R the width of the transformation zone associated with the crack. Addition of second-phase particles with a higher elastic modulus to TZP increases the elastic modulus of the composite E_c and consequently the fracture toughness.[1] The replacement of a certain amount of zirconia by a second-phase decreases the volume fraction V_i. So the product $E_c V_i$ in eqn (1) determines whether an increase in fracture toughness can be expected. Lange[1] found that an increase in fracture toughness can only be expected when the Young's modulus of the second-phase particle is at least twice as large as the Young's modulus of the Y-TZP. This is just the case for α-alumina as a second-phase addition. The elastic modulus of zirconia was reported to be in the range of 140 to 200 GPa.[2] The elastic modulus of alumina was reported to be 411 GPa.[3]

The increase in elastic modulus due to the addition of alumina also influences the retention of the tetragonal structure. According to Lange[4] the increase in elastic modulus of the constraining composite matrix increases the strain energy, thus lowering the constrained transformation temperature. In other words, the addition of alumina to Y-TZP enlarges the critical grain size for transformation of tetragonal particles, which was experimentally confirmed by Hou *et al.*[5]

Little experimental work has been done to investigate the effect of the addition of alumina on the mechanical properties of Y-TZP. It was found[6,7] that the addition of 20 wt% alumina resulted in a significant increase in strength and toughness. Furthermore the addition of 20 wt% alumina to Y-TZP was found[7] to improve the resistance to spontaneous phase transformation under the influence of water elevated temperatures.

The preparation of the above-mentioned composites has not been well described in the literature and is restricted to wet-milling zirconia and α-alumina,[8,9] or the hydrolysis of a homogeneous solution of metal nitrates with ammonia.[7] Although it was claimed[7,9] that a homogeneous distribution of alumina was obtained, this conclusion was not fully supported by micrographs.

The starting point of the work pesented in this paper is to disperse 20 wt% of alumina in a zirconia powder matrix with preservation of the excellent sintering behaviour of the zirconia powder matrix as reported by Theunissen *et al.*[10] This Y-TZP powder was obtained by the hydrolysis of a dilute solution of metal chlorides in a large excess of ammonia.[11] During non-isothermal sintering this Y-TZP powder reached 96% of the theoretical density at 1150°C with a ceramic grain size of 0·18 μm.[10] This preparation method, therefore, will serve as a starting point for the preparation of zirconia–alumina composite powders. The alumina will be homogeneously dispersed as a metastable transition alumina. The presence of transition aluminas is a consequence of the use of wet-chemical preparation techniques and calcination temperatures which are too low to form α-alumina. It has been shown in the literature[12,13] that during sintering the θ- to α-alumina phase transformation takes place at approximately 1240°C. This is considerably higher than the temperature at which the surrounding zirconia matrix is thought to reach a density of more than 95% of the theoretical density.[10] The θ- to α-alumina phase transformation is accompanied by a considerable shrinkage of the isolated alumina particles. This shrinkage must take place without breaking the contact with the surrounding zirconia matrix.

The question arises whether the use of transition alumina-containing composite powders can serve as a starting material for the preparation of Y-TZP/20 wt% α-alumina without increasing the sintering temperature necessary to obtain dense ceramics to a higher value than the temperature necessary to transform all θ-alumina particles (1240°C). Furthermore the question must be answered to what extent homogeneity is an important factor, especially with respect to differential sintering of any possible alumina aggregates.

In this paper several wet-chemical preparation techniques are presented which are believed to result in a homogeneous dispersion of 20 wt% alumina in Y-TZP. One of the preparation methods (the α-alumina method) involves the use of α-alumina instead of transition alumina in order to investigate whether the use of transition aluminas provides any advantage over the use of α-alumina. A fine-grained composite material has to be obtained by pressureless sintering, which offers the possibility of post-sintering heat treatments in order to obtain a tetragonal zirconia matrix with optimum mechanical properties. Furthermore, the ceramic grain size

has to be small in order to obtain a material suitable for hot-forging experiments.

2 Experimental Procedure

2.1 Powder preparation

Zirconia (+2–2·5 mol% yttria)/12–20 wt% alumina ceramic powders were prepared by four wet-chemical techniques: (1) the coprecipitation method, (2) the acetyl acetonate method, (3) the spraying method and (4) the α-alumina method. The α-alumina method also required the use of commercially available fine-grained α-alumina. The coprecipitation method was used to prepare a composite powder in which the Y-TZP contained 2 mol% yttria. The other preparation methods were used to prepare composite powders in which the Y-TZP contained 2·5 mol% yttria.

In the coprecipitation method the hydroxides were precipitated from one precursor solution in order to obtain an intimate mixture of both phases. This method involved the hydrolysis of a dilute solution (0·4 M) of aluminium chloride (Merck, extra pure), yttrium chloride (Cerac, 99·9%) and zirconium chloride (Merck, p.a.) in HCl (0·2 M) by adding it slowly to a large excess of NH_4OH (Merck, 25%). The hydrolysis was performed in a dispersion turbine reactor.[14] The hydrous gel was washed nine times in water/ammonia mixtures with decreasing amounts of ammonia, using a high-energy disc turbine, in order to remove all chloride. Between each washing step the gel was allowed to settle, after which the clear supernatant liquid was removed. During hydrolysis and subsequent washing the pH remained 11 or more in order to prevent recrystallization of the aluminium hydroxide, whose stability depends on pH. The gel was filtered and wet-milled with ethanol in polyethylene bottles using teflon balls. Subsequently the gel was washed three times with ethanol in the same reactor vessel as described for the water/ammonia washing in order to remove free water prior to drying. The gel was dried in air at 120°C, dry-milled in a polyethylene bottle using teflon balls and calcined in air at temperatures ranging from 550°C to 1000°C. Calcination involved a heating and cooling rate of 2·5°C/min whereas the ultimate calcination temperature was maintained for 2 hours.

Both the acetyl acetonate method and the spraying method involved the preparation of yttria-stabilized zirconia prior to the addition of alumina. The preparation of the yttria-stabilized zirconia involved the hydrolysis of a dilute solution (0·4 M) of zirconium chloride (Merck, p.a.) and yttrium chloride (Cerac, 99·9%) in HCl (0·2 M) in a large excess of ammonia, corresponding to the coprecipitation method as already described. The dried gel was used for the acetyl acetonate method, whereas the spraying method required a calcination procedure (550°C; 2 h) prior to the addition of the alumina.

The starting point of the acetyl acetonate method was the dispersion of alumina by mixing a hydrous zirconia/yttria gel with a solution of aluminium acetyl acetonate (Merck, >98%) in ethanol. The aluminium acetyl acetonate was dispersed by chemical adsorption of the organometallic compound on the zirconia surface.[15] In this case the aluminium acetyl acetonate reacts with the hydroxide groups of the hydrous zirconia/yttria gel, forming acetyl acetone as a by-product.[15]

In the acetyl acetonate method 70 g of $Al(AcAc)_3$ was completely dissolved in absolute ethanol (dried on molecular sieves) at a temperature of ±80°C. The dried zirconium (yttrium) hydroxide gel was added slowly to this hot solution and mixed thoroughly for several hours. The mixing was performed in a baffled beaker using a dispersion turbine. In this way optimum chemisorption of aluminium acetyl acetonate groups on the hydrated zirconia surface was obtained. The amount of ethanol was slowly reduced by evaporation. The remaining suspension was wet-milled for two weeks in a polyethylene bottle using teflon balls. The gel was dried for 15 h in air at 80°C followed by drying at 120°C for a few hours. The dried gel was milled in a polyethylene bottle using teflon balls and calcined in air at 500°C or 850°C for 2 h in order to decompose the precipitated aluminium acetyl acetonate and to transform the hydroxide into oxide. In one case calcination was performed under a continuous supply of oxygen.

In order to establish the importance of dissolving completely the aluminium acetyl acetonate prior to the addition of the hydroxide gel, in one case an ethanol suspension was prepared of aluminium acetyl acetonate and a hydrous zirconia/yttria gel (dried on molecular sieves). In this way relatively large aluminium acetyl acetonate particles may be present from the beginning. The suspension was wet-milled for ten days in a polyethylene bottle using teflon balls and further treated under the same procedure as mentioned previously.

The idea behind the spraying method was to increase the degree of dispersion of both alumina and zirconia and to prevent a large local supersaturation of the alumina precursor. This was done by spraying small droplets into dilute ammonia of a suspension containing zirconia and a dilute solution of aluminium chloride. The addition of the precursor to dilute ammonia was performed by spraying instead of adding it dropwise because of the smaller droplet size during spraying.

The spraying method involved the preparation of

a suspension of yttria-stabilized zirconia (25 g/litre) in a dilute solution (±0·1 M) of aluminium chloride (pH 2–3). The zirconia particles were prepared separately as described in this paper. After stirring for 1 h the suspension was subjected to an ultrasonic treatment in order to break down the zirconia agglomerates. In one case the pH of the suspension was adjusted to 1 h by addition of some hydrochloric acid prior to ultrasonification. Directly after ultrasonification the suspension was sprayed through a spraying nozzle into a beaker with dilute ammonia (1 M; pH ≥ 11) under continuously stirring. The gel was washed twice with dilute ammonia (1 M) in order to remove all chloride. The gel was filtered and wet-milled in ethanol in a polyethylene bottle using teflon balls. Subsequently the gel was washed and dried as previously described. The dried gel was calcined at 500°C for 2 h.

The idea behind the α-alumina method was to enclose a fine-grained commercial α-alumina powder (AKP 50, Sumitomo Chemical Co., Ltd) in a hydrous zirconia/yttria gel structure. According to the manufacturer this α-alumina powder has a particle size of 0·1–0·3 μm. The α-alumina method involved the preparation of a suspension of α-Al_2O_3 (3·83 g/litre) in a dilute solution (0·2M) of hydrochloric acid containing zirconium chloride (27·6 g/litre) and yttrium chloride (1·28 g/litre). After stirring the suspension was subjected to an ultrasonic treatment in order to break down all alumina agglomerates. Directly after ultrasonification the suspension was added slowly to a large excess of ammonia, corresponding to the coprecipitation method as already described. The washing procedure was the same as that of the coprecipitation method. The gel was dried in air at 120°C and calcined in air at 550°C for 2 h.

2.2 Characterization

Oxide powder suspensions used for the preparation of composite powders were subjected for 10 min to ultrasonification (65 W) using a Branson Sonifier 450. The particle size distribution of the suspensions was measured prior to hydrolysis using a Horiba LA-500 laser diffraction particle size distribution analyser (particle size range: 0·5–80 μm) or a Malvern autosizer 2c (particle size range: 0·2–0·8 μm).

Several techniques were used to characterize the chemical and phase compositions of the powders. X-Ray fluorescence spectrometry using a Philips PW 1410 spectrometer was used for the analysis of the chemical composition of the powders. A Philips PW 1710 X-ray diffractometer using CuK_α radiation was used to analyse the phase composition of the composite powders by continuous scanning from 2θ values of 14° to 80° with a scan speed of 0·05°/s.

The crystallization behaviour of zirconia during calcination was investigated by differential scanning calorimetry using a Stanton Redcroft DSC 1500. Heating was performed with a heating rate of 10°C/min under a continuous supply of nitrogen using α-alumina as a reference.

Powder compacts were obtained by isostatic compaction at 400 MPa. Powder compaction behaviour was investigated by measuring the density as a function of the isostatic pressure. Non-isothermal sintering behaviour was investigated using a Netzsch 402E dilatometer at a heating rate of 2·5°C/min. Densification behaviour of the prepared compacts was compared with commercially available Tosoh TZ-3Y20A (Toyo Soda Manufacturing Co., Ltd, Japan).

Nitrogen adsorption/desorption isotherms at −196°C were measured on green compacts using a Micromeritics ASAP 2400 after degassing the compacts at 300°C. The resulting pore size distributions were calculated from the desorption branch of the hysteresis loops. Pores with radii larger than approximately 15 nm were determined by mercury-intrusion porosimetry using a Carlo-Erba Porosimeter (Series 200). Specific surface areas of the powders were measured by means of nitrogen adsorption using the same Micromeritics ASAP 2400.

Bulk densities of the compacts were measured by the Archimedes technique (in mercury). Because of the difficulty in determining cell parameters of the transition aluminas all theoretical densities were based on α-alumina and tetragonal zirconia. The ceramic microstructure of polished and thermally etched compacts was examined using a Jeol JSM-35CF scanning electron microscope. Ceramic grain sizes were measured using the line intercept technique for measuring grain sizes in two-phase polycrystalline ceramics as described by Wurst & Nelson.[16]

3 Results and Discussion

3.1 Powder characteristics

It was found that the final chemical composition in almost all preparation methods deviated from 20 wt% alumina in Y-TZP (2–2·5 mol% Y_2O_3). The methods in which a suspension of an oxide powder (α-alumina in the α-alumina method and zirconia in the spraying method) was prepared resulted in a slightly lower content of the aluminium oxide which was in suspension (1–3 wt%). This was mainly due to sedimentation of large oxide particles in the suspension which were not used for the hydrolysis of the metal chlorides. Furthermore the acetyl acetonate method resulted in a considerably lower

Table 1. Powder characteristics and sintered density of Al_2O_3 dispersed in zirconia (+2–2·5 mol% yttria)

Synthesis method	$T_{calc.}$ (°C)	*Zirconia phase*	*Alumina phase*	S_{BET} (m^2/g)	*Sintered density*[a]
Coprecipitation	550	a	u	164	96[b]
	800	t	u	90	94[b]
	1000	t	u	18	95[b]
Acetyl acetonate	500	a	u	165	±60[c]
	850	t/(m)	u	60	98[c]
Spraying	500	t	u	135	95[c]
α-Alumina	550	t	α	60–80	98[c]
Tosoh[d]	—	t/(m)	α	16	98[c]

a = amorphous, m = monoclinic, t = tetragonal, u = unidentified. Phase in parentheses is minor phase.
[a] Percentage of theoretical density based on α-alumina and tetragonal zirconia.
[b] Sintered for 2 h at 1600°C.
[c] Sintered for 2 h at 1550°C.
[d] Data determined by authors.

alumina content (12–14 wt% Al_2O_3). In this case the alumina content proved to depend on the amount of powder (30–50 g) subjected to the heat treatment in order to decompose the aluminium acetyl acetonate. Small powder batches (4–15 g) resulted in the proper alumina content. The adsorption reaction of the aluminium acetyl acetonate might have been insufficient to adsorb all organometallic molecules on the support surface. The remaining part of the dispersed aluminium acetyl acetonate was probably partly evaporated because of insufficiently available oxygen present in the larger batches.

Table 1 summarizes some of the powder properties of the composite powders obtained. In all cases the alumina phase is unidentified, except where commercial α-alumina is used. In the case of low calcination temperatures (500–550°C) either amorphous zirconia or tetragonal zirconia is present. The powders containing amorphous zirconia were obtained by the preparation methods in which both zirconium/yttrium oxide and aluminium oxide were obtained in one calcination step (coprecipitation method; acetyl acetonate method). During calcination at high temperatures (800–1000°C) crystallization of the zirconia phase occurred. In this case the crystallization of amorphous zirconia to the tetragonal structure is clearly visible using differential scanning calorimetry (Fig. 1). The crystallization of zirconia in pure Y-TZP normally takes place at approximately 450°C.[10,17] In the presence of aluminium acetyl acetonate the crystallization shifts to 690°C. In the presence of aluminium hydroxide the crystallization temperature shifts to 790°C.

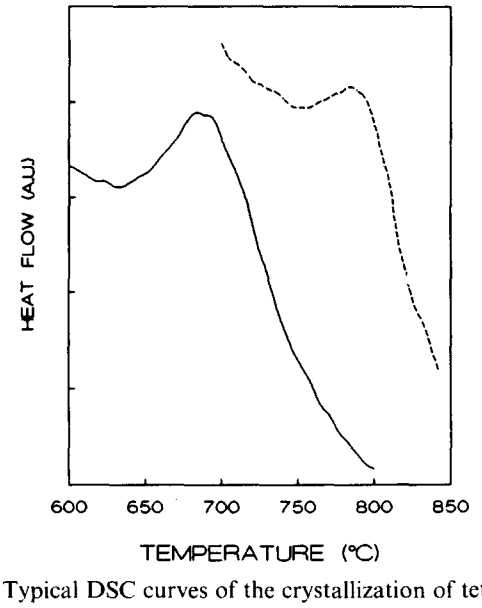

Fig. 1. Typical DSC curves of the crystallization of tetragonal zirconia in powders obtained by the acetyl acetonate method (——) and the coprecipitation method (------). Heating rate: 10°C/min.

Significant variations are obtained in the density after sintering (Table 1). The coprecipitation method results in a density of only 95% after sintering at a rather high temperature (1600°C). The same holds for the spraying method, although the sintering temperature is slightly lower (1550°C). The other preparation methods give a density of 98% after sintering at 1550°C with the exception of the powder prepared by the acetyl acetonate method and calcined at 500°C, which hardly densifies.

3.2 Green microstructure

Green compacts, after isostatic compaction at 400 MPa, obtained by the acetyl acetonate ($T_{calc.}$: 500°C) and spraying method ($T_{calc.}$: 550°C) showed a narrow pore size distribution with a mean pore radius of 3–4 nm. Only a tail of larger pores was observed in the green compacts with a pore radius in the range of 5–10 nm. The pore size distributions resemble those obtained for pure Y-TZP.[10]

The pore size distributions of the green compacts derived by the coprecipitation method are given in Fig. 2. The compacts calcined at 550°C and 800°C have a bimodal pore size distribution. The compact calcined at 1000°C, not shown in Fig. 2, on the other hand, yielded a very broad pore size distribution

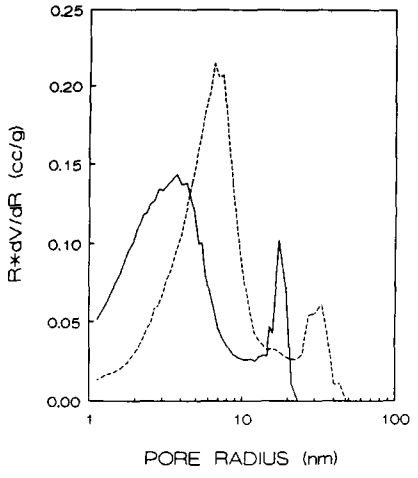

Fig. 2. Pore size distribution of a compact calcined at 550°C (———) and 800°C (- - - - -) obtained by the coprecipitation method.

with pores ranging from 4 to 210 nm. This large broadening of the pore size distribution is clearly due to the high calcination temperature. The mean pore radius of 4 nm in the compacts calcined at 550°C corresponds well to pore radii measured in pure Y-TZP obtained by an identical precipitation method.[10] The pores in the composite are the pores in a compact containing amorphous zirconia, whereas Ref. 10 was concerned with tetragonal zirconia ($T_{calc.}$: 550°C). The larger pores of 16 nm correspond well to pore radii observed in green compacts of zirconia-toughened alumina,[13] suggesting the latter to be pores between transition alumina aggregates.

3.3 Densification behaviour and ceramic microstructure

Typical densification curves upon heating for powder compacts derived by the coprecipitation method are given in Fig. 3. The difference in densification behaviour between the compacts calcined at 550°C and 1000°C is clearly demonstrated. Based on the densification rate the non-isothermal sintering of the compact calcined at 550°C can be divided into three temperature ranges. The first temperature range (600–800°C) with a maximum densification rate at 700°C is identified as being related to the crystallization of amorphous zirconia. The observed macroscopic densification may be caused by a change in density due to crystallization. Amorphous zirconia has a significantly lower theoretical density (by at least 10%) than tetragonal zirconia,[18] probably resulting in a macroscopic shrinkage of the compact upon crystallization. The second (800–1040°C) and third temperature ranges (1040–1550°C) represent the macroscopic densification behaviour of the composite material. The maximum in densification rate at 700°C, related to the crystallization of zirconia, was not observed for the compact calcined at 800°C.

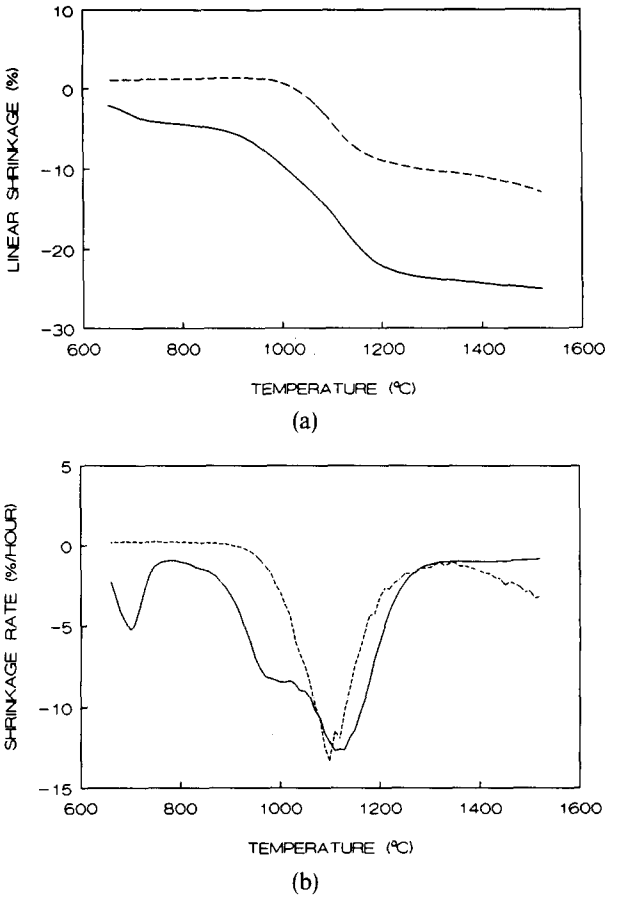

Fig. 3. Typical dilatometer curves of compacts obtained by the coprecipitation method and calcined at 550°C (———) or 1000°C (- - - - - -). Heating rate: 2·5°C/min. (a) Linear shrinkage, (b) shrinkage rate.

The densification behaviour of the compact calcined at 1000°C exhibits only one densification stage in the temperature range from 950°C to 1550°C with a maximum densification rate at 1100°C. In the latter sample densification still proceeds when reaching the maximum temperature (1550°C).

Scanning electron micrographs (Fig. 4) reveal that a bimodal distribution of alumina in the zirconia matrix is present in the compacts obtained by the coprecipitation method ($T_{calc.}$: 550°C) and sintered for 2 h at 1600°C. Alumina is present as spherical

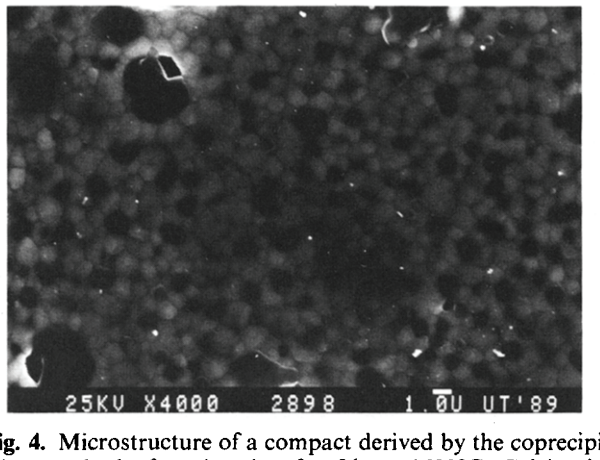

Fig. 4. Microstructure of a compact derived by the coprecipitation method after sintering for 2 h at 1600°C. Calcination temperature: 550°C.

aggregates and as individual particles with diameters of 6 and 1·3 μm, respectively. Both the alumina aggregates and alumina grains are homogeneously dispersed in the zirconia matrix with zirconia particles of approximately 1·8 μm in size. The spherical alumina aggregates are surrounded in part by large voids. This microstructure was independent of the calcination temperature.

As already suggested, the bimodal pore size distribution of the green compacts (Fig. 2) obviously is due to pores within the matrix material and to pores between the alumina aggregates. The latter is only possible when these aggregates form larger clusters. It is, therefore, believed that larger transition alumina aggregates were already present in the green compact which resulted from the coprecipitation method. These aggregates exhibit a different densification behaviour to that of the surrounding composite matrix. Densification of these aggregates starts at approximately 1100°C when the densification behaviour of these aggregates resembles that of pure transition alumina.[19] The maximum densification rate will be at approximately 1150°C, after which the transition to α-alumina phase transformation inhibits further densification of these aggregates.[19] Sintering to full density of these aggregates is to be expected at 1450°C. The zirconia matrix which surrounds the alumina aggregates is expected to sinter to full density in the temperature range from 1000°C to 1300°C. The small maximum in densification rate at 1000°C may reflect the onset of this matrix densification. The larger maximum in densification rate at 1150°C is due to the superposition of the densification of the alumina aggregates and the densification of the zirconia matrix. A higher calcination temperature (1000°C) causes the densification stages to coincide.

According to the densification curves a high density is already obtained at 1250°C when the densification stops. According to the expected local densification behaviour of the alumina aggregates these aggregates still exhibit a significant porosity.[19] Further densification of the alumina aggregates is to be expected, while the matrix has already reached a high density. It is at this stage that upon further heating the large circumferential voids are formed around the spherical-like alumina aggregates[20] which are clearly visible in Fig. 4. These voids account for the relatively low density after sintering (Table 1).

A typical densification curve of a compact containing 14 wt% alumina derived by the usual acetyl acetonate method is presented in Fig. 5. Because powders calcined at 500°C hardly showed any macroscopic densification no curve is presented for this case. Macroscopic densification of the compacts calcined at 500°C was only observed

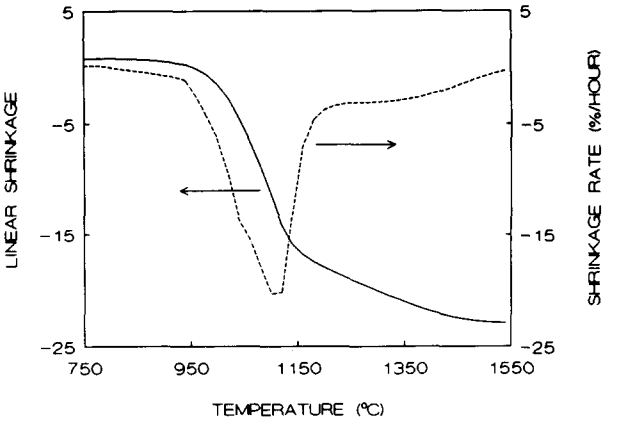

Fig. 5. Typical dilatometer curve of compact derived by the acetyl acetonate method, calcined at 850°C. Heating rate: 2·5°C/min. (———) Linear shrinkage, (- - - - -) shrinkage rate.

above 1450°C. Macroscopic densification of the compacts calcined at 850°C already starts at approximately 950°C (Fig. 5). The maximum densification rate is observed at approximately 1100°C and is identified as being due to the sintering of the zirconia–transition alumina composite as a whole. As can be seen in Fig. 5 the densification rate drastically decreases upon further heating above the temperature of the maximum in densification rate (1100°C), although some densification is still observed until a temperature of approximately 1450°C is reached and densification practically stops. Isothermal sintering experiments at 1200°C showed that within 10 h a density of 94% of theoretical density could be obtained.

A typical microstructure of a dense compact (1550°C, 2 h) obtained by the acetyl acetonate method is depicted in Fig. 6. Spherical-like alumina particles, which clearly are not polycrystalline aggregates as in the case of the coprecipitation method, are homogeneously dispersed throughout the zirconia matrix. The alumina particles are 1·5 μm in size, whereas the zirconia particles are 1 μm in size. Because no large alumina aggregates are present the absolute value of the shrinkage (10%) accompanying

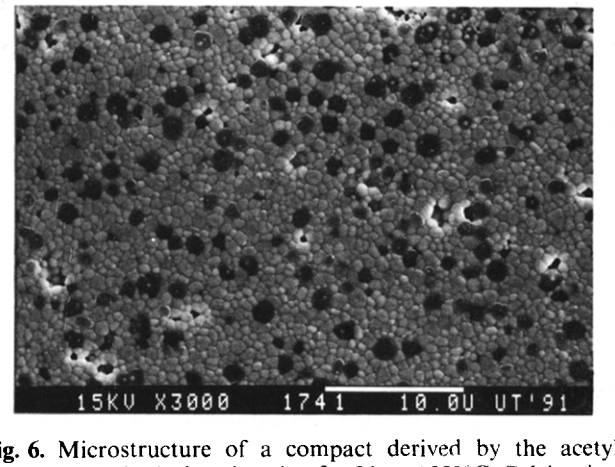

Fig. 6. Microstructure of a compact derived by the acetyl acetonate method after sintering for 2 h at 1550°C. Calcination temperature: 850°C.

the transition-alumina to α-alumina phase transformation is relatively small, in comparison to the coprecipitation method, and can more easily be compensated by the Y-TZP matrix. The response of the Y-TZP matrix to the phase transformation results in the extra macroscopic densification observed at higher temperatures (1200–1350°C).

The preparation of a solution of aluminium acetyl acetonate prior to the addition of the zirconia/yttria hydroxide gel proved to be a very important step in the distribution of the alumina phase. When the alumina was derived from an aluminium acetyl acetonate suspension inhomogeneities in phase composition were observed on a small scale ($< 5\,\mu m$) and on a larger scale ($> 100\,\mu m$).

As already mentioned the coprecipitation and the acetyl acetonate method represent preparation methods where both zirconium/yttrium oxide and aluminium oxide are obtained in one calcination step, resulting in amorphous zirconia when calcined at low temperatures (500–550°C). The difference between these preparation methods is that composites containing amorphous zirconia obtained by the coprecipitation method and calcined at a low temperature can be sintered to full density, whereas in the case of the acetyl acetonate method hardly any densification takes place. Although no satisfying explanation is available it must be emphasized that both preparation methods result in a different crystallization behaviour of the zirconia phase. Any explanation of the difference in sintering behaviour will probably be related to this phenomenon.

The spraying method involved the preparation of a suspension of yttria-stabilized zirconia in an aluminium chloride solution in water. After ultrasonic treatment a zirconia particle size of approximately $10\,\mu m$ is obtained. The addition of some hydrochloric acid in order to adjust the pH to 1, prior to ultrasonification (65 W, 10 min) further decreased the zirconia particle size in the suspension to $2–3\,\mu m$.

The macroscopic densification of the compacts obtained by the spraying method starts at approximately 850°C. Densification proceeds up to 1550°C and two maxima in densification rate are observed (Fig. 7). The first maximum is observed at 1100°C, whereas the second maximum is observed at 1200°C. Upon further heating densification is inhibited and a significantly higher temperature is required in order to start further densification.

The spraying method results in a microstructure as shown in Fig. 8. The alumina grains ($2\,\mu m$) are clearly not homogeneously distributed through the zirconia matrix. The alumina particles seem to be distributed around zirconia clusters and are accompanied by significant porosity. The zirconia grain size within the clusters is approximately $1\,\mu m$,

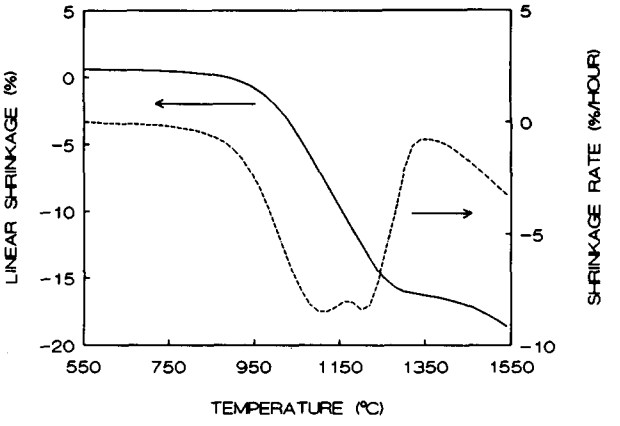

Fig. 7. Typical dilatometer curve of a compact derived by the spraying method. Heating rate: 2·5°C/min. (———) Linear shrinkage, (------) shrinkage rate.

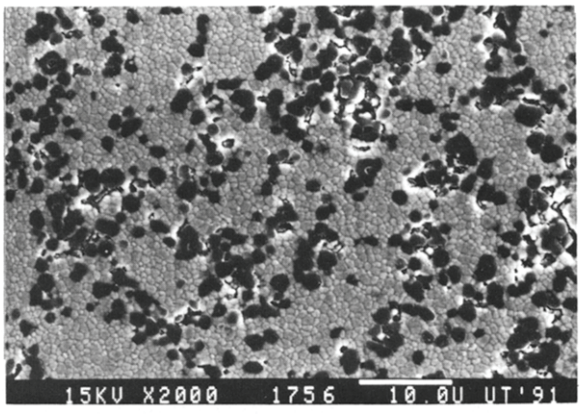

Fig. 8. Microstructure of a compact derived by the spraying method after sintering for 2 h at 1600°C.

whereas the clusters are approximately $10\,\mu m$ in size. The size of the zirconia clusters corresponds well with the agglomerate size of the zirconia in the suspension prior to hydrolysis.

The addition of some hydrochloric acid prior to ultrasonification of the suspension in order to further break down the zirconia particle size resulted in a more homogeneous distribution with zirconia clusters of approximately $3\,\mu m$, which corresponds well with the agglomerate size of the zirconia in that suspension. It is, therefore, concluded that the aluminium hydroxide is not formed within the zirconia agglomerates but only around the agglomerates. The maximum in densification rate at 1100°C (Fig. 7) obviously reflects the densification of the zirconia clusters, whereas the maximum in densification at 1200°C, which is superimposed on the first maximum, is due to an extra contribution of the alumina particles to the macroscopic densification. From this it follows that any improvement of the microstructure by the spraying method requires a further breakdown of the zirconia agglomerates in the suspension prior to the hydrolysis of the alumina precursor.

The α-alumina method involved the preparation of a suspension of α-alumina in a dilute solution of

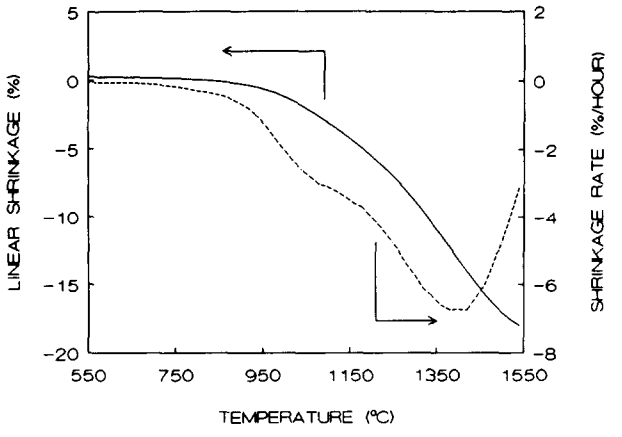

Fig. 9. Typical dilatometer curve of a compact obtained by the α-alumina method. Heating rate: 2·5°C/min. (———) Linear shrinkage, (------) shrinkage rate.

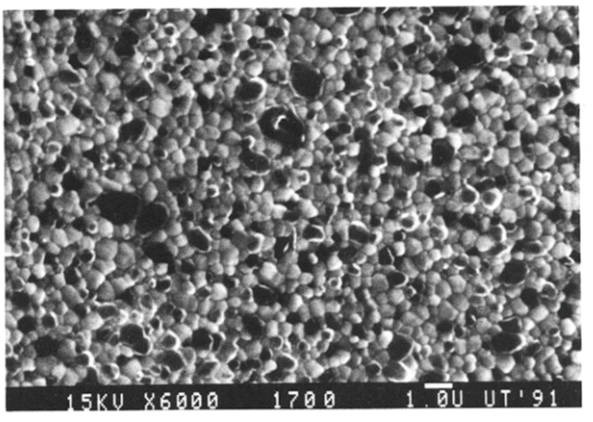

Fig. 10. Microstructure of a compact derived by the α-alumina method after sintering at 1550°C (dwell at this temperature is zero).

zirconium chloride and yttrium chloride prior to hydrolysis. Ultrasonification proved to be very effective in diminishing the α-alumina particle size in the suspension. After ultrasonification a median particle size of 0·45 μm is obtained while almost all particles are below 1 μm. A densification curve of a compact obtained by the α-alumina method is depicted in Fig. 9. Macroscopic densification starts at approximately 950°C and proceeds up to 1550°C. The maximum in densification rate is observed at 1400°C. This maximum reflects the contribution of the zirconia–α-alumina composite matrix which obviously densifies at a much higher temperature than is the case for the zirconia–transition alumina composites obtained by the other preparation methods. Obviously zirconia–alumina composites containing only 20 wt% α-alumina sinter to full density at much higher temperatures than composites containing the same amount of transition alumina (Figs 3 and 7). Isothermal sintering experiments at 1450°C showed that within 2 h a density of more than 95% of theoretical density could be obtained.

The α-alumina method exhibits a homogeneous distribution of the alumina particles throughout the Y-TZP matrix. Most alumina particles are ≤ 1 μm in size with only a small number of particles ranging from 1 to 2 μm. The small α-alumina particle size results from the fact that the powder is easily deagglomerated. The zirconia matrix is fine-grained with a zirconia grain size of 0·8 μm (Fig. 10). The zirconia grain size is less than observed for compacts obtained by the acetyl acetonate method (1 μm). The difference is probably due to a difference in dwell time during isothermal sintering at 1550°C, which was 2 h for the acetyl acetonate method and 0 h for the α-alumina method.

The densification behaviour of Tosoh TZ-3Y20A is depicted in Fig. 11 and largely resembles the densification behaviour as described for the spraying method (Fig. 7). Significant macroscopic densification upon heating is observed to start at 950°C. Densification proceeds up to 1550°C, and two maxima in the densification rate are observed. The first maximum in the densification rate is observed at 1100°C and the second maximum is observed at 1250°C. In contrast with the spraying method the densification rate slowly decreases with increasing temperature instead of increasing again at high temperatures (1550°C).

Tosoh TZ-3Y20A has a microstructure which is less homogeneous compared with the acetyl acetonate and the α-alumina method (Fig. 12). The alumina particles, with sizes in the range of 0·5 to 1 μm, are rather irregularly shaped and, especially in comparison to the α-alumina method, less homogeneously distributed. This is an important observation because Tosoh TZ-3Y20A is considered worldwide to be an excellent powder for composite materials.

The starting point of the work presented in this paper is to prepare dense ceramics in which 20 wt% of α-alumina is homogeneously dispersed in a fine-grained (±0·5 μm) zirconia matrix. The latter requires preservation of the excellent sintering behaviour of the zirconia matrix powder as reported

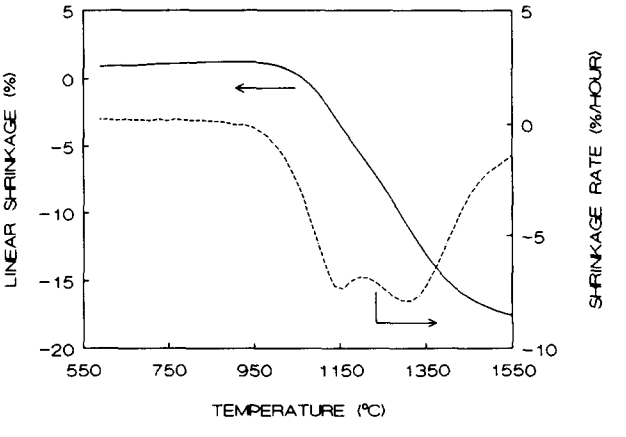

Fig. 11. Typical dilatometer curve of Tosoh TZ-3Y20A. Heating rate: 2·5°C/min. (———) Linear shrinkage, (------) shrinkage diameter rate.

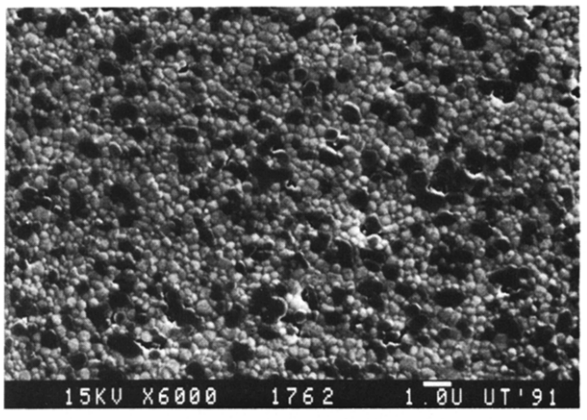

Fig. 12. Microstructure of Tosoh TZ-3Y20A after sintering for 2 h at 1400°C.

by Theunissen *et al.*[10] Both the coprecipitation method and the spraying method result in a relatively low density (95%) which proves to be due either to differential sintering of alumina aggregates (coprecipitation method) or to an inhomogeneous distribution of the alumina phase (spraying method).

Both the acetyl acetonate and the α-alumina method result in high density (98%) ceramics in which the alumina is homogeneously distributed throughout the Y-TZP matrix. Neither of these preparation methods fully satisfy all the conditions. In contrast with the α-alumina method, the acetyl acetonate method did not result in the required amount of alumina. Powder compacts obtained by the acetyl acetonate method exhibit a maximum in densification rate at 1100°C, whereas compacts obtained by the α-alumina method exhibit a maximum in densification rate at 1400°C. The acetyl acetonate method, therefore, allows sintering temperatures (1200–1300°C) which are considerably lower than in the case of the α-alumina method (1450°C). Provided that the dwell time during isothermal sintering of compacts obtained by the acetyl acetonate method at 1200–1300°C is equal to that necessary to densify compacts obtained by the α-alumina method at 1450°C, the lower sintering temperature for the acetyl acetonate method will result in much smaller zirconia grains. The zirconia grain size (0·8 μm) in the sintered compacts obtained by the α-alumina method is still sufficiently small to stabilize the tetragonal structure. Both the grain sizes of alumina and zirconia in this compact are relatively large for hot-forging experiments.

4 Conclusions

Composite powders containing 12–20 wt% alumina dispersed in Y-TZP have been prepared by several wet-chemical preparation techniques. Both the acetyl acetonate and the coprecipitation method resulted in a shift in the crystallization temperature of amorphous to tetragonal zirconia towards 690°C (acetyl acetonate method) or 790°C (coprecipitation method).

The spraying method and the coprecipitation method resulted in a relatively low density (95%) after sintering at temperatures ranging from 1550°C to 1600°C. These relatively low densities resulted from differential sintering of transition alumina aggregates of ±6 μm in size (coprecipitation method) or from an inhomogeneous distribution of the alumina phase (spraying method).

After sintering for 2 h at 1550°C the acetyl acetonate method gave a much more homogeneous distribution of the alumina (1·5 μm) in a Y-TZP matrix (1 μm), although a significantly lower alumina content (12–14 wt%) was obtained. Isothermal sintering experiments at 1200°C showed that within 10 h 94% of the theoretical density could be reached. These lower sintering temperatures probably result in smaller grain sizes.

The α-alumina method exhibited a homogeneous distribution of alumina (1 μm) in a fine-grained Y-TZP matrix (0·8 μm) but required a much higher sintering temperature (1450°C) than the composites containing transition alumina as a starting phase. Both the acetyl acetonate method and the α-alumina method gave better results in homogeneity than those obtained with the Tosoh powder.

Acknowledgement

The research was partly supported by the Innovative Research Programme on Technical Ceramics (IOP-TK) with financial aid of the Dutch Ministry of Economic Affairs.

References

1. Lange, F. F., Transformation toughening. Part 2: contribution to fracture toughness. *J. Mater. Sci.*, **17** (1982) 235–9.
2. Stevens, R., *An Introduction to Zirconia.* Magnesium Elektron, Litho 2000, Twickenham, UK, 1986, p. 1.
3. Crandall, W. B., Chung, D. H. & Gray, T. J., The mechanical properties of ultra-fine hotpressed alumina. In *Mechanical Properties of Engineering Ceramics*, ed. W. W. Kriegel & H. Palmour. Interscience Publishers, New York, London, 1961, pp. 349–76.
4. Lange, F. F., Transformation toughening. Part 4: fabrication, fracture toughness and strength of Al_2O_3–ZrO_2 composites. *J. Mater. Sci.*, **17** (1982) 225–34.
5. Hou, Y.-Y., Gao, J.-Q. & Zhang, H.-T., Effect of Al_2O_3 on retaining tetragonal particles in Y-PSZ ceramic matrix. *J. Mater. Sci. Lett.*, **6** (1987) 246–8.
6. Tsukuma, K., Ueda, K. & Shimada, M., Strength and fracture toughness of isostatically hot-pressed composites of Al_2O and Y_2O_3-partially-stabilized ZrO_2. *J. Am. Ceram. Soc.*, **68** (1985) C4–C5.
7. Rajendran, S., Swain, M. V. & Rossell, H. J., Mechanical properties and microstructures of co-precipitation derived tetragonal Y_2O_3–ZrO_2–Al_2O_3 composites. *J. Mater. Sci.*, **23** (1988) 1805–12.
8. Sato, T., Fujishiro, H., Endo, T. & Shimada, M., Thermal

stability and mechanical properties of yttria-doped tetragonal zirconia polycrystals with dispersed alumina and silicon carbide particles. *J. Mater. Sci.*, **22** (1987) 882–6.
9. El-Sayed Ali, M., El-Houte, S. & Sørensen, O. T., Preparation and mechanical properties of ceria doped tetragonal zirconia/alumina ceramics. In *Structural Ceramics: Processing, Microstructure and Properties*, ed. J. J. Bentzen, J. B. Bilde-Sørensen, N. Christiansen, A. Horsewell & B. Ralph. Risø National Laboratory, Roskilde, Denmark, 1990, pp. 263–8.
10. Theunissen, G. S. A.M., Winnubst, A. J. A. & Burggraaf, A. J., Sintering kinetics and microstructure development of nanoscale Y-TZP ceramics. *J. Eur. Ceram. Soc.* (in press).
11. Groot Zevert, W. F. M., Winnubst, A. J. A., Theunissen, G. S. A. M. & Burggraaf, A. J., Powder preparation and compaction behaviour of fine-grained Y-TZP. *J. Mater. Sci.*, **25** (1990) 3449–55.
12. Den Exter, P., Leuwerink, T. H. P., Bos, A., Winnubst, A. J. A., Doesburg, E. B. M. & Burggraaf, A. J., Preparation and characteristics of zirconia/alumina ceramic powders. In *Euro-Ceramics*, Vol. 1, *Processing of Ceramics*, ed. G. de With, R. A. Terpstra & R. Metselaar. Elsevier Applied Science, London, 1989, pp. 89–93.
13. Leuwerink, T. H. P., Den Exter, P., Winnubst, A. J. A. & Burggraaf, A. J., Characteristics of wet chemically prepared alumina/zirconia ceramics. In *Materials Science Monographs, 68: Advanced Structural Inorganic Composites*, ed. P. Vincenzini. Elsevier Science Publishers, 1991, pp. 619–28.
14. Van de Graaf, M. C. A. G., Ter Maat, J. H. H. & Burggraaf, A. J., Microstructure and sintering kinetics of highly reactive ZrO_2–Y_2O_3 ceramics. *J. Mater. Sci.*, **20** (1985) 1407–18.
15. Van Ommen, J. G., Hoving, K., Bosch, H., van Hengstum, A. J. & Gellings, P. J., The preparation of supported oxidic catalysts by adsorption of metal acetylacetonates, $M(acac)_n$, on different supports. *Z. Phys. Chem. N.F.*, **134** (1983) 99–106.
16. Wurst, J. C. & Nelson, J. A., Lineal intercept technique for measuring grain size in two-phase polycrystalline ceramics. *J. Am. Ceram. Soc.*, **55** (1972) 109.
17. Mercera, P. D. L., Zirconia as a support for catalysts; preparation, characterization and properties. PhD Thesis, University of Twente, Enschede, The Netherlands, 1991.
18. Crucean, E. & Rand, B., Calcination of zirconia gels. *J. Brit. Ceram. Soc.*, **78** (1979) 58–64.
19. Den Exter, P., Winnubst, A. J. A. & Burggraaf, A. J., The pressureless sintering and sinter forging of zirconia toughened alumina. *J. Am. Ceram. Soc.* (submitted).
20. Evans, A. G., Considerations of inhomogeneity effects in sintering. *J. Am. Ceram. Soc.*, **65** (1982) 497–501.