

2.5Y-TZP from Yttria-Coated Pyrogenic Zirconia Nanopowder

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Abstract

Thanks to their high strength and toughness, yttria-stabilized zirconia polycrystals (Y-TZP) have become one of the most important structural ceramics for engineering and biomedical applications. In this study 2.5Y-TZP powder was produced from monoclinic pyrogenic nanopowder with a nitrate coating and calcination process. The powders were consolidated by hot pressing to obtain specimens for mechanical testing, phase analysis and microstructural investigation. Bending strength, toughness, microstructure and transformability of the nano-TZP were determined depending on sintering temperature in the range 1300–1500 °C. The materials produced showed a combination of high toughness (9–10 MPa·√m) and strength (1000–1200 MPa). While the toughness showed little variation with sintering temperature, the best strength was observed at low sintering temperatures with materials of extremely fine grain size.

Keywords: zirconia, nanopowder, hot-pressing, powder coating, Y-TZP

1. Introduction

A comprehensive overview on zirconia materials and their toughening mechanisms was given by Hannink¹. The high strength and toughness of zirconia ceramics is based on their ability to undergo a stress-induced martensitic transformation from tetragonal to monoclinic, which is associated with a volume increase and shear. Zirconia structural ceramics can be divided into two main groups. Partially stabilized zirconia (PSZ) grades like Mg-PSZ and Ca-PSZ include tetragonal precipitates in a large grain size cubic matrix. TZP materials consist of tetragonal polycrystals of grain sizes from 0.1 – 3 μm depending on the type of stabilizer used. While Y-TZP usually leads to materials of high strength and moderate toughness, Ce-TZP is extremely tough at moderate strength levels. Strength and toughness are apparently inversely correlated as shown by Swain². Incorporation of second phases into the zirconia matrix can lead to materials with enhanced strength and toughness. Tsukuma³ obtained ATZ (alumina-toughened zirconia) with a strength up to 2.4 GPa. Jiang⁴ has presented results on Y-TZP/WC composites with a strength of 2 GPa and high toughness. In order to boost the toughness of Y-TZP, several strategies can be pursued, long-time annealing to grow the grains as shown by Ruiz⁵, reducing the yttria content either in the coprecipitated powder⁶ or by blending⁷ and finally powder coating^{8,9}. The first three methods are associated with severe problems in long-term stability especially in moist environment¹⁰. Y-TZP qualities with large grains or low yttria content are more prone to spontaneous transfor-

mation than fine grain materials with an yttria content above a certain threshold. Lange¹¹ has shown that the minimum yttria content to keep a TZP ceramic tetragonal depends on grain size. He has, however, also shown that toughness in TZP is related to the size of the transformation zone (in most cases the grain size). It was therefore commonly believed that ultrafine grain TZP ceramics are brittle. Singh et al.¹² could show that using plasma-produced coated powders can lead to extremely tough materials despite fine grain sizes. Burger⁸ showed that coated powders have a better densification behaviour, superior strength and toughness compared to coprecipitated powders. The benefit of such fine microstructures in biomedical applications was demonstrated by Piconi et al.¹³. They could show that Y-TZP from coated powder not only offers finer microstructures but also a higher stability towards hydrothermal degradation. Unfortunately, coated powders are no longer commercially available. Yuan⁹ has shown that, at least on lab- or pilot-plant-scale, powder coating with yttrium nitrate solution and subsequent calcination can yield yttria-coated powders of good quality. The method has also been adapted to produce other coated powders like Ce-TZP¹⁴ or Nd-Y-TZP¹⁵. Another technology based on yttrium trichloride can be performed without calcination but requires extensive washing to eliminate the chloride adsorbed on the powder. Vasilkiv¹⁶ and Mayo¹⁷ have presented results on the consolidation of coprecipitated nano-Y-TZP. To our knowledge, no one has either attempted to produce coated powders from ultrafine pyrogenic zirconia or to measure strength depending on heat treatment temperature. Exist-

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ing literature has focused on the evolution of hardness and toughness – probably due to the limited size of the produced samples. In order to obtain additional application-relevant information on the influence of processing conditions a commercially available pyrogenic monoclinic nanopowder of 12 nm primary crystallite size was coated by the nitrate route and samples of sufficient size for a complete mechanical characterization were produced.

II. Experimental

The powder coating process was performed as described by Yuan⁹ with slight modifications due to the fine grain size of the nanopowder used. 95.63 g of monoclinic zirconia (VP-PH, Evonik, Germany) with a primary crystallite size of 12 nm and a BET surface area of $60 \pm 15 \text{ m}^2/\text{g}$ (manufacturer's data) was dispersed in 500 g of n-propanol. The slurry was transferred to a 1000-cm³ polyethylene flask and 200 cm³ of Y-TZP milling balls of 5 mm in diameter were added. 4.37 g of yttria (99.9%, Sigma Aldrich, USA) were dissolved in 50 ml of boiling half-concentrated nitric acid in a magnetic stirrer. The yttrium nitrate solution was then diluted to 200 cm³ and added to the zirconia slurry. The flask was sealed and rotated for 24 h at 20 rpm by an electric drive unit. After the milling balls had been removed, the solvent was evaporated at 110 °C. The dried coated powder was crushed in a mortar and subsequently calcined in air in an alumina crucible at 800 °C for 1 h. The calcined powder was then crushed again, screened through a 200- μm screen and attrition-milled twice. First for 1 h in 200 g propanol at 500 rpm with 5-mm Y-TZP balls, then for 1 h with 1-mm balls. In order to obtain the ready-to-press feedstock, the powder was dried in air at 90 °C and screened through a 100- μm screen.

Hot pressing (KCE, Germany) was performed in a 40-mm diameter circular graphite die. For each disk 14 g of powder was used in order to obtain disks of $\sim 1.6 - 1.8 \text{ mm}$ thickness after grinding. The disks in contact with the powder were coated with boron nitride suspension. After the die had been placed in the press, the pressing chamber was evacuated to 0.1 mbar. Heating was performed at 50 K/min to 1150 °C, the load of 60 MPa was applied and the sample was predensified for 10 min before heating to final temperatures at 20 K/min. The final temperatures were 1300 – 1500 °C with 50 K increments. Heat soaking time was 1 h in each case. The heater was then switched off and the sample cooled down in the press under argon atmosphere. The hot-pressed disks were then ground with a 40- μm diamond disk and polished with 6- μm and 1- μm diamond suspension on both sides (Struers Rotopol, Germany). 6 bending bars of 4 mm in width were cut from each sample with a diamond wheel (Struers Accutom 50, Germany). The sides and edges of the bending bars were bevelled with a 40- μm diamond disk and subsequently polished with 15- μm diamond suspension to remove defects induced by cutting. 3-point bending tests were performed according to DIN EN 6872 with 15-mm span.

Hardness and toughness as well as the Archimedes density were measured on the remaining pieces of the disk. Microhardness HV0.1 and Young's modulus were determined from the loading/unloading curve according to the universal hardness method with a microindenter (Fischerscope, Germany). Hardness HV10 was measured with a Vickers indenter (Bareiss, Germany), applying the load for 10 s. Fracture toughness was determined with the indentation method after Niihara¹⁸ and Anstis¹⁹ to enable comparison with available literature data. The microstructure of the samples was investigated by means of SEM with low acceleration voltage of 3 kV (Jeol, K6300, Japan) on polished and thermally etched (Air, 1225 °C/1 h) surfaces without conductive coating. Grain sizes were determined from SEM images of 20000x magnification (not shown) according to the line intercept method by counting the number of grain boundaries on five lines of known length and correcting with a geometry factor as shown by Mendelson²⁰. The phase composition of powders, polished and ground samples was determined by X-ray diffraction (XRD) with Co K α radiation without monochromator (Bruker AXS D8 Advance, Germany) according to the calibration curve determined by Toraya²¹. The transformability was calculated as the difference between the monoclinic content of ground (125- μm diamond disk) and polished samples. The cubic fraction was estimated from the ratio between cubic (111), tetragonal (101) and monoclinic peaks (111) and $(\bar{1}11)$.

III. Results and Discussion

(1) Powder analysis

The XRD pattern of as-received and coated powder is shown in fig. 1. The as-received “monoclinic” zirconia is in fact partially tetragonal (65.8 % monoclinic). This is a result of the rapid quenching of the small crystallites after flame pyrolysis. After the coating and annealing treatment, the powder turns predominantly monoclinic (96.6 % monoclinic).

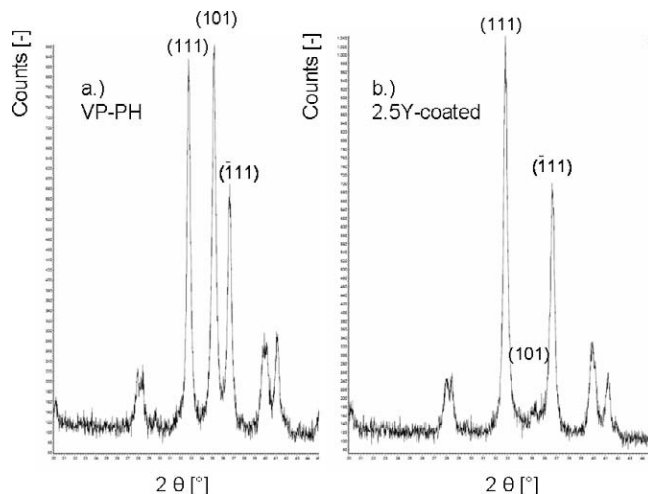


Fig. 1: a.) XRD pattern of as-received Evonik VP-PH b.) XRD pattern of 2.5Y coated VP-PH after annealing at 800 °C/1h; 2 θ -range 20–45°.

(2) Mechanical properties

As expected, the hardness as well as the Young's modulus (fig. 2) of the samples slightly decreases with higher sintering temperature owing to increasing grain sizes and thus following the Hall-Petch equation. Bending strength and fracture toughness after Niihara's equation are shown in fig. 3.

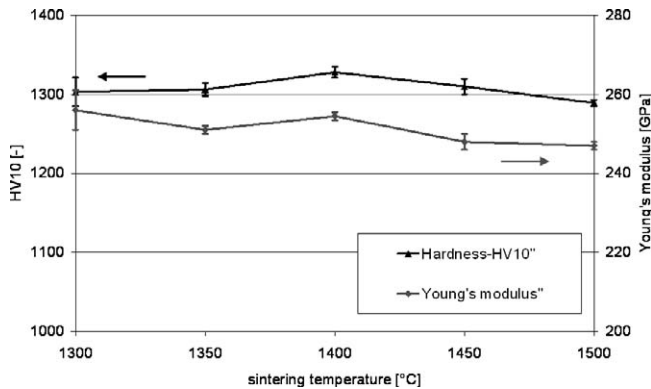


Fig. 2: Hardness HV10 and Young's modulus of 2.5Y-TZP vs. sintering temperature.

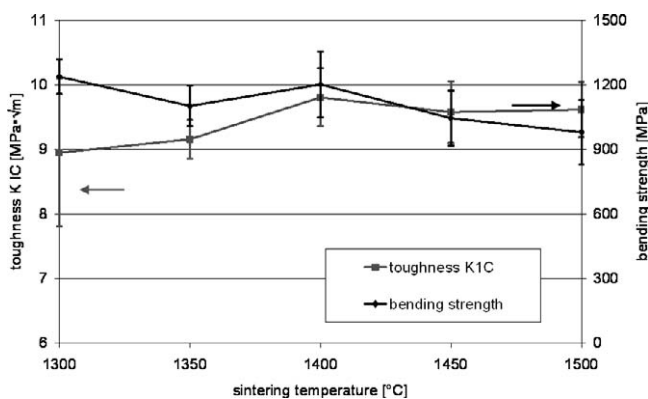


Fig. 3: Bending strength and fracture toughness of 2.5Y-TZP vs. sintering temperature.

Fracture toughness reaches quite a high value of 9-10 MPa·√m. K_{IC} rises slightly with increasing sintering temperatures and reaches its maximum at 1400 °C before declining. The bending strength shows a different tendency. The highest strength of > 1200 MPa is reached at 1300 °C sintering temperature; it almost stays at this level up until 1400 °C and then declines to 1000 MPa at 1500 °C. The best combination of toughness and strength is obtained at a sintering temperature of 1400 °C. At this temperature the material thus reaches the limits of strength/toughness correlation defined by Swain². Strength and toughness values are respectable but not spectacular. The data show that the coated 2.5Y TZP has a quite broad and reliable processing range from 1300-1400 °C sintering temperature. Growing the grains by increasing the sintering temperature is inefficient to increase the toughness of Y-TZP from coated powder, an observation already made by Singh¹² with Ti oxide YZ860 powder.

(3) Microstructure and phase composition

Figs. 4-8 show the microstructures of thermally etched TZP sintered at 1300-1500 °C. Fig. 9 shows the evolution

of mean grain size and density with increasing sintering temperature. The mean grain size of the TZP stays unchanged at 320-330 nm in the sintering temperature range from 1300 to 1400 °C. Grain size runs up to 480 nm up-

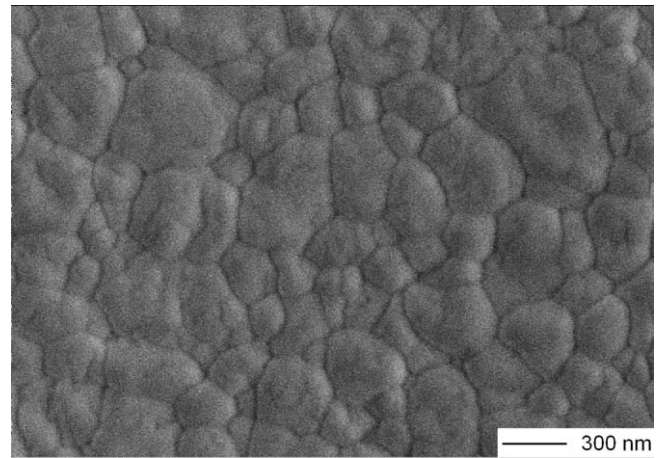


Fig. 4: Microstructure of 2.5Y-TZP sintered at 1300 °C/1 h.

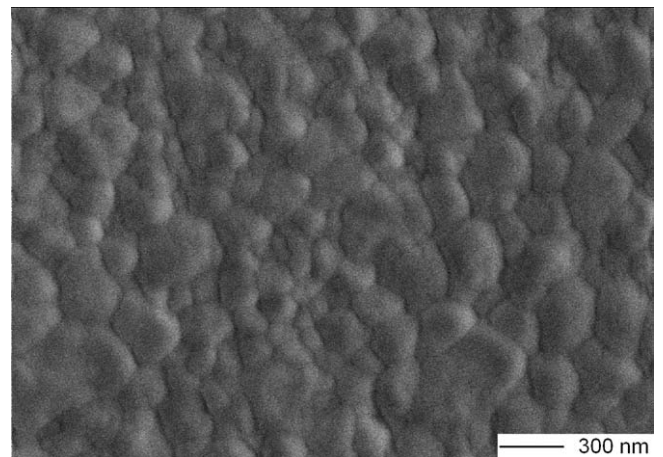


Fig. 5: Microstructure of 2.5Y-TZP sintered at 1350 °C/1 h.

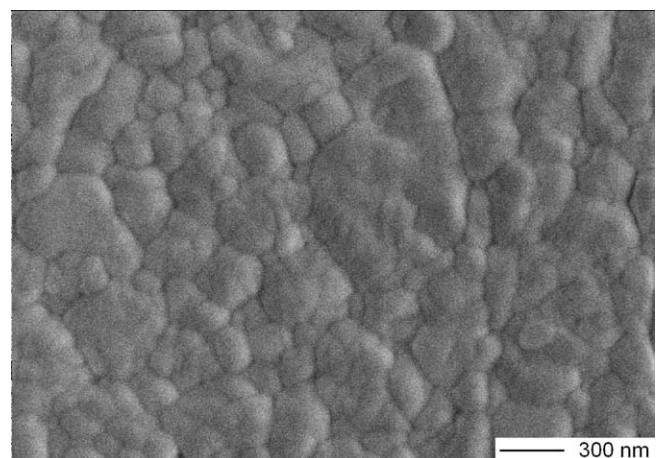


Fig. 6: Microstructure of 2.5Y-TZP sintered at 1400 °C/1 h.

on further increase to 1450 °C but stays at this value at 1500 °C sintering temperature. This discontinuous rise in grain sizes leads to the assumption that it is linked to the process of yttria diffusion from the surface to the bulk of the grains. Grain growth presumably starts once this redistribution process is completed. Singh¹² demonstrated that

the grain size distribution in 2.5Y coated tioxide powder is extremely bimodal at temperatures as low as 1350 °C. Oversize cubic grains are distributed in a matrix of fine tetragonal grains. In case of the pyrogenic powder this behaviour was not observed to the same extent. Grain size distribution is more continuous, a size gap between 0.3 and 1 µm cannot be observed. Grain sizes hardly exceed 500 nm at sintering temperatures < 1400 °C.

The decline in density of the sample sintered at 1500 °C as well as the high content of abnormally large grains (fig. 8) hint at a large content of cubic phase, but the density of 5.96 g/cm³ does not fit. This value would mean a cubic phase content of 25 %, which is much too high even for 3Y-TZP. The surface texture of these large grains looks very different to the sample in fig. 7 sintered at 1450 °C with the same average grain size. Elevations in large grains look as if the grains were falling apart into smaller units. This behaviour may be caused by phase transformation.

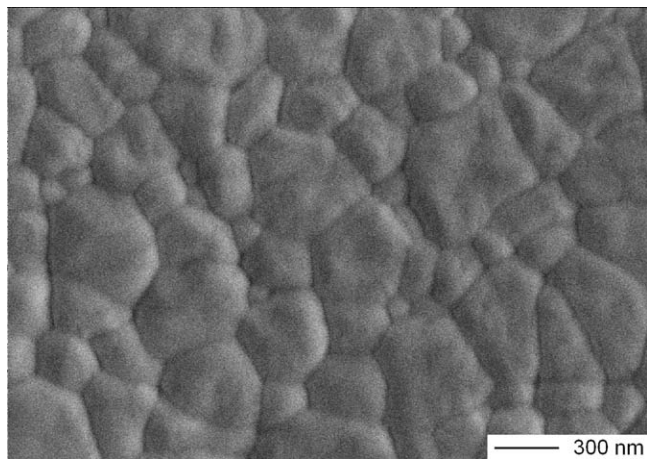


Fig. 7: Microstructure of 2.5Y-TZP sintered at 1450 °C/1 h.

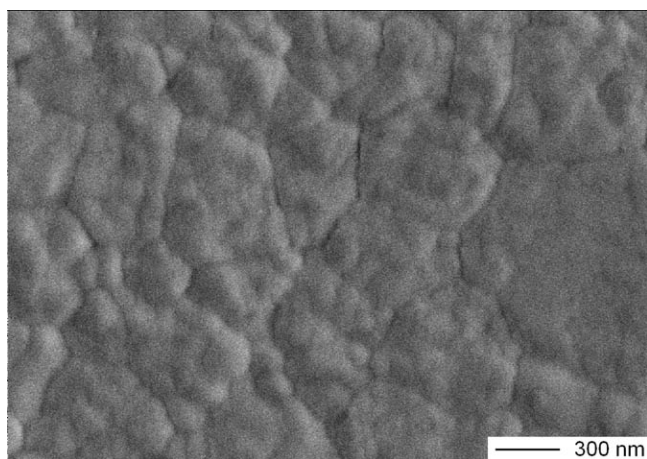


Fig. 8: Microstructure of 2.5Y-TZP sintered at 1500 °C/1 h.

2.5Y-TZP is slightly under stabilized and according to Lange¹¹ reaches a critical limit for transformation at 0.5 µm grain size. Fig. 9 shows that this threshold value is reached at 1450 °C. It is, however, unlikely that the larger grains, which are supposedly cubic grains containing high fractions of yttria, should transform to monoclinic. As the monoclinic content of the 1500 °C samples is not extraordinarily high, this uncommon aspect of large grains

may be caused by cubic to tetragonal transformation upon cooling.

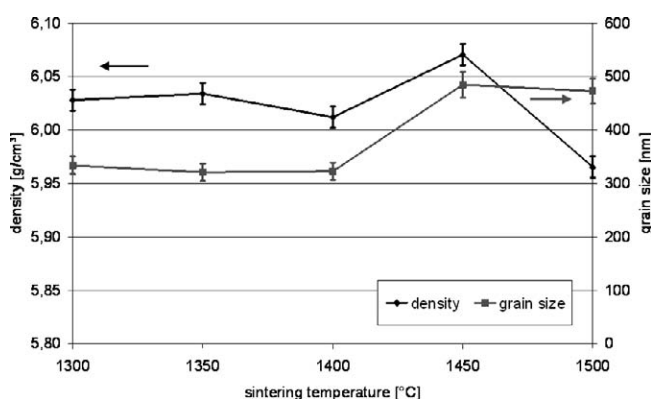


Fig. 9: Archimedes' density and grain size of 2.5Y-TZP vs. sintering temperature.

Fig. 10 shows the results of XRD analysis of ground and polished samples. The phase analysis delivers additional information for understanding the strength and toughness relationships observed. The transformability of the zirconia rises with increasing sintering temperature and reaches its peak value at 1450 °C. At 1500 °C the transformability decreases. The shape of the transformability curve does not match the toughness curve in fig. 3. Another point worth discussing is the fraction of cubic zirconia plotted in fig. 11. The reason for the monoclinic volume fraction increase in the 1300-1350 °C temperature range is not clear.

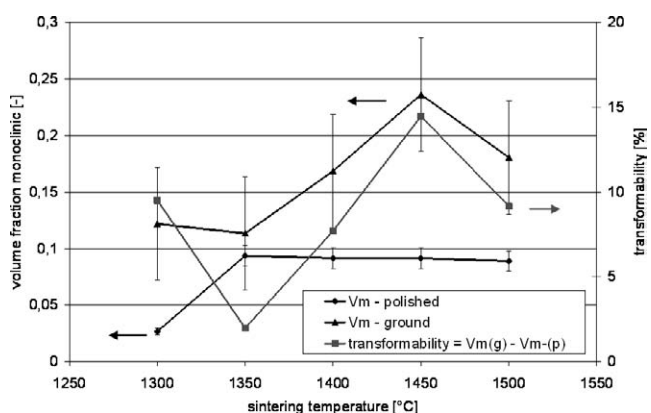


Fig. 10: Phase analysis of ground and polished samples vs. sintering temperature.

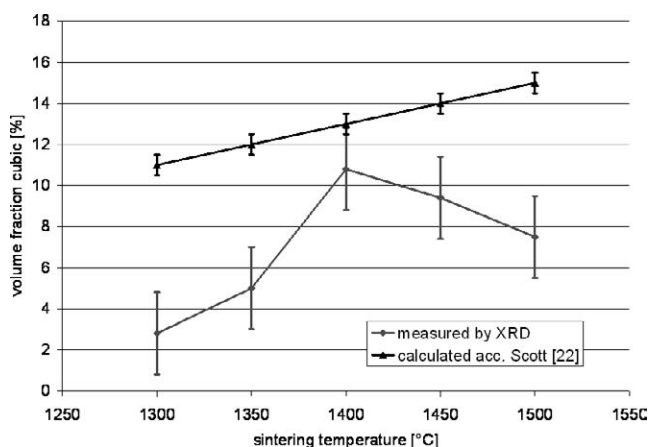


Fig. 11: Cubic fraction of 2.5Y-TZP measured by XRD and calculated from phase diagram.

The cubic fraction grows from < 3 % at 1300 °C to 12 % at 1400 °C and then comes down to < 8% again at 1500 °C. The equilibrium composition at final sintering temperature calculated from the phase diagram by Scott²² is plotted for comparison. It is quite easy to explain the lower cubic content at lower sintering temperatures. Yttria is initially present as a homogeneous coating surrounding the monoclinic grains. During heating, grains grow and thermally activated yttria diffusion takes place to form first predominantly tetragonal and finally increasing fractions of cubic solid solution. XRD analysis reveals that at high temperatures cubic phase content is lower than expected. As the samples were not quenched and cooling was performed in the press at ~ 10 K/min, the metastable cubic grains may retransform to tetragonal. We have as yet no explanation why the cubic content at 1400 °C is almost the theoretical value (respecting error bars). Yttria redistribution from the surface to the bulk as well as between grains seems completed and apparently little metastable cubic phase is present at this temperature.

Cross checking the phase analysis results with the results of density measurements showed that the results were consistent within measuring errors of ± 1 %, except for the sample sintered at 1500 °C, which showed a lower density than expected from the cubic and monoclinic content. According to the rule of mixture in order to obtain a density of 5.96 g/cm³ measured, 25 % of cubic or monoclinic phase (density of ~ 5.65 g/cm³) together with 75 % of tetragonal phase (density ~ 6.05 g/cm³) should be present, however, only 16.5 % cubic+monoclinic were observed in XRD analysis. Porosity was not detected. This strange behaviour can only occur if the surface composition of the polished sample does not coincide with the composition of bulk of the as-fired sample (which determines the density). Sheu²³ reported cubic \rightarrow t' phase transformation of Y-TZP upon polishing. However, most of the compositions investigated by Sheu were closer to the tetragonal + cubic phase boundary and the samples were remelted and not sintered. This and the size of the grains in the 1500 °C sample give rise to the assumption that the grains were cubic after sintering and before surface treatment (polishing and etching), but appear tetragonal in XRD. The observed cubic phase content corresponds to the thermodynamic equilibrium value expected at ~ 1100 °C according to the phase diagram by Scott²².

It is known that t' phase does not transform to monoclinic²⁴, thus the loss in transformability at 1500 °C might be explained. As it is not possible to investigate as-fired surfaces of hot-pressed samples due to contamination of carbon and boron nitride, it was not possible to verify this a priori assumption.

It is known that cubic grains accumulate yttria and make the neighbouring tetragonal grains more transformable. This also seems to contribute to the peak in toughness at 1400 °C (fig. 3). An additional contribution may come from microcracking especially at high sintering temperature where larger monoclinic grains can be present.

IV. Summary and conclusion

Ultrafine pyrogenic zirconia powders were successfully coated by means of the nitrate route. The resulting

ceramics produced by hot pressing show a combination of high strength and toughness and extremely fine microstructures. The exact mechanisms taking place during sintering of coated Y-TZP powder have not been fully investigated yet. Different authors claim different mechanisms for toughening, in this study the correlation with strength was investigated for the first time, the improvements in mechanical properties compared to coprecipitated powders is obvious. Optimum mechanical properties were obtained at sintering temperatures between 1300 and 1400 °C. Higher heat treatment temperatures led to a deterioration of strength while toughness remains almost unaffected. Results shown in this study are more similar to results obtained on coated plasma-sprayed tioxide powder¹² than to those obtained on coated precipitated tosoh powder⁹. The powders from high-temperature synthesis seem more reactive and reach high toughness values at lower temperatures.

Further improvements of mechanical properties can be expected by addition of small amounts of alumina. Vleugels reported that this improves the mechanical properties of coated Y-TZP²⁵. Tsubakino²⁶ showed that alumina addition increases hydrothermal stability.

From an engineering point of view the hot-pressing process is generally quite unattractive and uneconomical as only simple geometries can be produced and ceramic components need to be manufactured from blanks by final machining. The low bulk density of the pressing feedstocks limits the size of pressed parts. 4-mm-thick samples require a pressing stroke of 15 mm even after precompaction. Applying SPS technology would increase the productivity but not solve the basic problem. While the present study has shown high potential owing to the favourable mechanical properties, a technical application of the powders does not seem feasible in the present state. Development of more sophisticated compounding technologies and – probably even more importantly – improved powders with higher bulk density would help to overcome the processing-related limitations.

Acknowledgements

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