J Mater Sci (2008) 43:1599–1611
DOI 10.1007/s10853-007-2343-x

Production and characterization of ZrO_2 ceramics and composites to be used for hip prosthesis

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Received: 6 April 2007 / Accepted: 27 November 2007 / Published online: 25 December 2007

Abstract Tetragonal ZrO_2 polycrystalline (TZP) ceramics with varying yttria and ceria content (2–3 mol%) and distribution (coated or co-precipitated), and varying second phase content Al_2O_3 were prepared and investigated by means of microstructural analysis, mechanical properties, and hydrothermal stability, and ZrO_2-based composites with 35–60 vol% of electrical conductive TiN particles were developed. The effects of stabilizer content and means of addition, powder preparation, sintering conditions, and grain size have been systematically investigated. Fully dense Y-TZP ceramics, stabilized with 2–3 mol% Y_2O_3, 2 wt% Al_2O_3 can be achieved by hot pressing at 1,450 °C for 1 h. The hydrothermal stability increased with increasing overall yttria content. The jet-milled TiN powder was used to investigate the ZrO_2–TiN composites as function of the TiN content. The experimental work revealed that fully dense ZrO_2–TiN composites, stabilized with 1.75 mol% Y_2O_3, 0.75 wt% Al_2O_3, and a jet-milled TiN content ranging from 35 to 60 vol% could be achieved by hot pressing at 1,550 °C for 1 h. Transformation toughening was found as the primary toughening mechanism. The decreasing hardness and strength could be attributed to an increasing TiN grain size with increasing TiN content, whereas the decreasing toughness might be due to the decreasing contribution of transformation toughening from the tetragonal to monoclinic ZrO_2 phase transformation. The E modulus increases linearly with increasing TiN content, whereas the hydrothermal stability increases with addition of TiN content.

Introduction

Zirconia can be used for orthopedic implants because of its chemical inertness and for refractory application because of its thermal shock resistance and abrasion resistance [1, 2]. Tetragonal zirconia-stabilized ceramics are candidate materials for surgical implants. The most important requirement of a biomaterial must be the tissue of the body and the material existing without any inappropriate effect on each other and remaining there for a period of time like for long-term application prosthesis, until the end of life time [3]. A major drawback of zirconia ceramics is their strength reduction, due to an unfavourable tetragonal to monoclinic martensitic phase transformation, with time when they are in contact with physiological fluids. The $t \rightarrow m$ transform is a reversible martensitic transformation, associated with a large temperature hysteresis (around 200 °C), a finite amount of volume change (4–5%) and a large shear strain (14–15%), which leads to crumbling of the sintered part made of pure zirconia during cooling [4]. It has been found that zirconia shows transformation toughening mechanism that exhibits resistance to crack propagation and the transformation toughening is influenced by the grain size, the grain size distribution and the stabilizer content [5].

The tetragonal phase in zirconia ceramics can be obtained by using yttrium or cerium oxide stabilizers. Yttria is the most popular stabilizer used for zirconia ceramics for its excellent mechanical properties, wear

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properties, and a good effect on tetragonal phase transformability. Studies have shown that yttria-stabilized ZrO_2 ceramics can exhibit more than 1,000 MPa strength, and about 6–10 Mpa $m^{1/2}$ toughness [5]. CeO_2-stabilized tetragonal polycrystals (Ce-TZP) are known as exhibiting higher fracture toughness than Y-TZP as 5–16 Mpa $m^{1/2}$ which can be due to difference in grain size, and has attracted interest [6, 7]. Also wear properties depend on starting powders, hardness and toughness, grain size and distribution, porosity, and experimental parameters [8].

In some cases, possible reduction of Ce^{+4} to Ce^{+3} during sintering in non-oxidizing atmosphere, can cause destabilization of the t-ZrO_2 phase [7]. The yttria- and ceria-stabilized ZrO_2 ceramic powders are mostly prepared by co-precipitation and sintering. It has been reported that using starting powders produced by coating technique has attracted considerable attention in recent years. It has been reported that Y_2O_3-coated ZrO_2 starting powders exhibit better mechanical properties than co-precipitate powders. The addition of small amounts of alumina has been reported to modify the grain boundaries, suppress grain growth, and increase the hardness and fracture toughness of stabilized TZP materials [9]. After sintering stabilized zirconia ceramics, normally tetragonal phase is obtained; the transformation into monoclinic phase could be due to some kind of energy addition by elastic or chemical effect. The energy is due to grain sizes, grain shapes, temperature, humidity, oxygen vacancy concentration, thermal expansion anisotropy, residual stress and microstructure [2]. From the different experiments on low temperature degradation in Y-TZP, the conclusions are such as; the transformation at room temperature is slow and the maximum rate is about 200–300 °C; the transformation is faster in water or water vapor; the transformation starts on the surface and extends into the sample and this situation is followed by micro-cracking and loss in strength [1, 5]. Transformation starts from the surface (polished wearing surface and interior of the cone in femoral heads) in the isolated grains by a stress corrosion because of the disequilibrium state of the grains. This disequilibrium state can be because of larger size of the grains, lower yttria content, a specific orientation from the surface and the presence of residual stresses [10]. During ageing the properties of degradation are due to the metastable tetragonal crystals into stable monoclinic structure transformation. A recent investigation has shown that the transformation occurs via a nucleation and growth mechanism where growth depends on some microstructural patterns such as porosity, residual stress, grain size, etc. [5]. Process stages effect the microstructure potentially like initial powders effecting stabilizer content and distribution leading to secondary phases [10]. It has been shown that the transformation begins with the nucleation on a grain, progresses to the neighbour grains, and micro-cracking and stresses occur. During ageing, in certain types of TZP ceramics, the tetragonal-monoclinic transformation can be an advantage of the creation of monoclinic phase-compressive surface layer which improves the mechanical properties, although ageing can be the cause of deterioration. Ageing tests can be done at temperatures higher than 37 °C [10]. It has been calculated that 1 h of autoclave testing at the temperature of 134 °C has theoretically the same effect as 3–4 years in the body [5]. The results of ageing are roughening which will be the cause of increased wear and micro-cracking which will be the cause of grain pull-out and possible failure [11].

Recent developments in zirconia composites are not only on the improvement of toughness, strength, and hardness, but also on the possibility for mass production and manufacturing cost reduction. The use of tetragonal zirconia polycrystals for wear applications is limited for their modest hardness, even though they have excellent mechanical properties [12]. They studied the influence of the addition of electrically conductive reinforcements such as TiB_2, $TiC_{0.5}N_{0.5}$, TiN, and TiC secondary phases on the microstructure and mechanical properties of Y-TZP. The incorporation of a certain content of these conductive reinforcements makes the composite electrically conductive enough to be machinable, thus avoiding the expensive grinding operation by final shaping and surface finishing of components [13].

The objective of this study is; to investigate whether the powder preparation and processing route influences the hydrothermal degradability behavior and mechanical properties of Y-TZP, and Y-Ce-TZP materials; to investigate whether the hydrothermal degradability of Y-TZP-based materials can be limited by the addition of a hard secondary, electrically conductive phase (TiN) to the Y-TZP matrix. Moreover the addition of TiN to a Y-TZP matrix has several advantages such as; the hardness and wear resistance of the Y-TZP material is improved, since pure TiN has a higher hardness (1,400 kg/mm^2) compared to Y-ZrO_2 (1,200 kg/mm^2); the machinability of the composite product is improved since the addition of at least 35 vol% of electrically conductive TiN to a Y-TZP matrix permits the material to be machined [13]; TiN is known to be biocompatible and will therefore improve the applicability of the composite material as surgical implant.

Experimental procedure

The compositions of the starting powders used to prepare the Y_2O_3 stabilised as co-precipiteated and coated, and Y_2O_3–CeO_2 stabilised as co-precipitated ZrO_2 powder-based ceramics are summarized in Tables 1 and 2. The zirconia powders were commercially available. They were yttria-free monoclinic ZrO_2 (Tosoh grade TZ-0, Japan) and 3 mol% yttria co-precipitated ZrO_2 (Tosoh grade TZ-3Y, Japan). Baikowski grade SM8 (France) Al_2O_3 powder was also used in small amounts as a grain growth inhibitor and sintering aid.

Yttria-stabilized ZrO_2–TiN composites with 35–60 vol% and 0.75 wt% Al_2O_3 were investigated. Mixed ZrO_2–TiN–Al_2O_3 samples were obtained as prepared for a previous study [12], no powder preparation technique or sintering was applied to the composite samples. According to this study, details on the commercial starting powders are given in Table 3. The commercial powders were yttria-free monoclinic ZrO_2 (Tosoh grade TZ-0), 3 mol% yttria co-precipitated ZrO_2 (Tosoh grade TZ-3Y) and jet-milled TiN (Kennametal, USA). The co-precipitated Y_2O_3 stabilizer content of the powder mixtures was adjusted by mixing the appropriate ratio of ZrO_2 starting powders. Al_2O_3 powder of 0.75 wt% (Baikowski grade SM8) was added as a ZrO_2 grain growth inhibitor and sintering aid to all composite grades. The composite samples were prepared by hot pressing at 1,550 °C for 1 h, except 60/40-0.75 TM1.75-TiN which was hot-pressed at 1,450 °C for 1 h.

Table 1 Powders and chemicals used

Material	Supplier	Remarks
Y_2O_3	AEE	99.9%
CeO_2	Merck	1–4 × 10^3 μm
Al_2O_3	Baikowski grade SM8	0.6 μm
ZrO_2	Tosoh grade TZ-0	0.05–0.1 μm
	Tosoh grade TZ-3Y	

Table 2 ZrO_2 starting powders

Material grade	Supplier	Y_2O_3 content (mol%)	Al_2O_3 content (wt%)	Grain size[a] (nm)
TZ-O	Tosoh	0	0.1	27
TZ-3Y	Tosoh	3	0.1	27

[a] According to the supplier datasheets

Table 3 Starting powders of the composites

Powder	Grade	Supplier	Crystal size[a]
ZrO_2	TZ-0	Tosoh	27 nm
ZrO_2	TZ-3Y	Tosoh	27 nm
TiN	Jet-milled	Kennametal	1.03 μm
Al_2O_3	SM8	Baikowski	0.60 μm

[a] According to the supplier datasheets

Y_2O_3 and CeO_2–Y_2O_3-co-precipitated ZrO_2 samples were prepared with the addition of 1 g Al_2O_3. In order to eliminate the ZrO_2 powder agglomerates in the starting powder, 150 g Y-TZP milling balls (Tosoh TZ-3Y ¢ = 5 mm) are added to the 50 g ZrO_2 powder containing ethanol suspension that was mixed on a multidirectional mixer (Type Turbula) for 24 h in a 250 mL polyethylene container, followed by drying in a rotating evaporation (Eyela) at 95 °C and for Y-Ce-TZP samples, drying in a furnace at 80 °C to remove the ethanol. The Y_2O_3 coating is formed by mixing the stabilizer salts in aqueous solution together with an organic solvent such as ethanol and monoclinic ZrO_2 nanopowder. The stabilizer salt and yttrium nitrate, were obtained by dissolving commercially pure Y_2O_3 in nitric acid. Ethanol suspension with well-defined $Y(NO_3)_3$ addition was mixed on the mixer for 24 h. After drying, the powders are calcined at 800 °C for 1 h to convert the nitrates into oxides. The calcined stabilizer-coated ZrO_2 nanopowder was crushed in an agate crucible using an agate mortar. After calcination, the powder was remixed and dried. Sample formulations are given in Table 4. Sample formulations of ZrO_2–TiN materials are given in Table 5 according to the previous study [13].

In order to densify the powder compacts, dried powder was pre-shaped in the graphite hot press die set-up in cold press at 40 kN, the pre-pressed compact was sintered in the FCT hot press (W 100/150-2200-50 LAX, FCT, Rauenstein, Germany) in vacuum ($\approx$0.1 Pa) at 1,450 °C during 1 h under a mechanical load of 40 kN. Hot pressing temperature cycle was with a heating rate of 50 °C/min, a dwell time of 1 h, and a cooling rate of 10 °C/min. The Ce-Y-TZP powders were shaped into small cylinders first by cold pressing at 10 MPa, then by cold isosatic pressing at 200 MPa (American Isostatic Press Inc. CP630) for 5 min, and sintering was performed at 1,450 °C for 1 h in a muffle furnace (Nabertherm) in air at a heating rate of 20 °C/min from 25 °C to 1,000 °C and 10 °C/min from 1,000 °C to 1,450 °C, and cooling was performed at 10 °C/min.

Cross-sectioned samples were ground and polished for hardness and indentation toughness measurements, as well as XRD and thermally etched in air at 1,350 °C for 30 min for Scanning Electron Microscopy (SEM) analysis. The density of the sintered samples was determined according to the Archimedes principle (BP210S balance, Sartorius AG, Germany) and by pycnometer (Quantachrome Ultrapycnometer 100). The E-modulus of the samples was determined by the resonance frequency method using a device operating on the principles of the impulse-excitation technique (Model Grindo-Sonic, J. W. Lemmens N.V., Leuven, Belgium). The hardness was determined by Vickers indentation (Model FV-700, Future-Tech Corp., Tokyo, Japan, and Wolpert 2Rc) with a load of 10 kg. The

Table 4 Sample formulations of Y-TZP and Y-Ce-TZP materials

Composition	Yttria content (mol%)	Yttria source	Ceria content (mol%)	Ceria source	Alumina content (wt%)	Alumina source
ZrO_2–Al_2O_3 (TM2-SM8)	2	Co-precipitated TZ-3Y	–	–	2	By mixing
ZrO_2–Al_2O_3 (TM2.5-SM8)	2.5	Co-precipitated TZ-3Y	–	–	2	By mixing
ZrO_2–Al_2O_3 (TM3-SM8)	3	Co-precipitated TZ-3Y	–	–	2	By mixing
ZrO_2–Al_2O_3 (TM2-coated)	2	By coating	–	–	2	By mixing
ZrO_2–Al_2O_3 (TM2.5-coated)	2.5	By coating	–	–	2	By mixing
ZrO_2–Al_2O_3 (Ce2-TM3-SM8)	3	Co-precipitated TZ-3Y	2	Co-precipitated CeO_2	2	By mixing
ZrO_2–Al_2O_3 (Ce3-TM2-SM8)	2	Co-precipitated TZ-3Y	3	Co-precipitated CeO_2	2	By mixing

Table 5 Sample formulations of Yttria stabilized ZrO_2–TiN composites[a]

Ceramic grade	Yttria content (mol%)	Yttria source	Al_2O_3 content (wt%)	Alumina source
65/35-0.75 TM 1.75-TiN (1 h—1,550 °C)	1.75	Co-precipitated	0.75	By mixing
60/40-0.75 TM 1.75-TiN (1 h—1,550 °C)	1.75	Co-precipitated	0.75	By mixing
60/40-0.75 TM 1.75-TiN (1 h—1,450 °C)	1.75	Co-precipitated	0.75	By mixing
50/50-0.75 TM 1.75-TiN (1 h—1,550 °C)	1.75	Co-precipitated	0.75	By mixing
40/60-0.75 TM 1.75-TiN (1 h—1,550 °C)	1.75	Co-precipitated	0.75	By mixing

[a] Data is taken from previous study [13]

microstructure of the starting powders and densified cross-sectioned ceramic grades was studied by scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands, and JEOL JSM 7000F). XRD (Seifert 3003 T/T, Ahrensburg, Germany, and Rigaku Miniflex) analysis was used for phase identification and calculation of monoclinic and tetragonal ZrO_2 phase content before hydrothermal treatment.

For the wear experiments, ball-on-plate configuration was prepared and 10-mm diametre Alumina balls were used as counterbodies. The experiments were performed on a computer controlled tribometer (CSM Ins. Tribometer) at room temperature 23–25 °C; relative humidity measurement at 41–45%. Hyaluronic acid liquid (20 mg/2 mL hyaluronic acid sodium salt, FIDIA S.p.A., Italy) was used as lubricant to simulate joint synovial fluid. Fretting vibration at the contacts was activated by a linear relative displacement of constant stroke (4 mm) as flat samples mounted on a translation table reciprocating with 1.59 Hz frequency, 10,000 cycle, load of 5 N and speed of 2 cm/s. The friction coefficient was calculated from the computer-measured tangential force. All the tests were performed with identical parameters to make comparison. Microstructural characterizations of the worn surfaces on as polished samples and ball were done by Optical Profilometer (Veeco Wyko NT1100) and SEM (Jeol JSM 7000F).

Hydrothermal treatment was applied to the samples by placing the samples in a stainless steel container as autoclave using salt bath to vaporize water. The temperature measurement was done by means of a thermocouple. The samples were heated, respectively, for total of 5 min, 10 min and 20 min at 200 °C. The salt bath liquid is a commercial one 93/112/EG, AS 140 with the proper shipping name potassium nitrate and sodium nitrite mixture from the firm, Houghton Benelux b.v., with the melting point of 207 °C (according to the supplier data sheets). Cooling was done manually by removing the autoclave out of the furnace and quenching in water. These heating steps were done for all the samples, up to 3 cycles of,

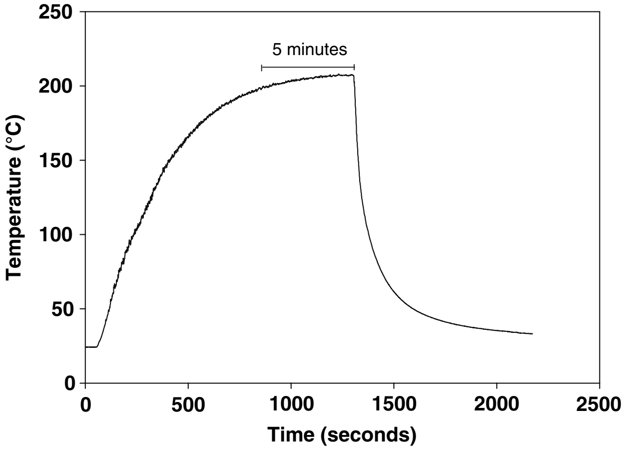


Fig. 1 Typical hydrothermal cycling curve

respectively, 5, 5 and 10 min dwell time when the temperature of the autoclave reached 200 °C in the salt bath. The cycling curve is shown in Fig. 1. At the end of each step, XRD analysis for phase identification was used to follow the transformation and calculate the monoclinic and tetragonal phase content.

Results and discussion

Microstructures

Yttria stabilized ZrO_2 ceramics were hot pressed for 1 h at 1,450 °C and Yttria-Ceria stabilized ZrO_2 ceramics were cold pressed at 200 Mpa and sintered for 1 h at 1,450 °C. SEM has been used to investigate the influence of the processing route and the stabilizer and alumina content on the grain size of the ZrO_2 ceramics. Representative micrographs of polished cross-sectioned of the different thermally etched ZrO_2 material grades are represented in Figs. 2 and 3. Two phases can be differentiated, i.e. ZrO_2 (grey), and Al_2O_3 (black). The microstructural investigation of the samples revealed that all samples were fully densified since no porosity could be observed. Homogeneous ZrO_2 microstructures were obtained. The grains in all the investigated ceramics are fairly equiaxed whereas the small grains which are predominant, are tetragonal. It is known that the grain sizes of Y-TZP materials increases with increasing sintering temperature [9]. Also it can be observed that in the existence of small amounts of alumina, small grain size can be achieved.

SEM Micrographs on polished and thermally etched surface showed that the large ZrO_2 grains are rich in ceria content, because of the difference in the grain size and distribution of CeO_2. The larger grain size in 2Y-3Ce material is due to these large ZrO_2 grains, and also grain size decreases with increasing yttria content up to 2–3 mol%. It is known that addition of small amounts of Al_2O_3 to a T-ZP matrix acts as a grain growth inhibitor and a sintering aid, enhancing densification during pressureless sintering and controlling the transformability and toughness of the material through tetragonal ZrO_2 grain size control [14].

In order to have more detailed information on the grain size the grain size distribution was measured using Image Pro Plus Analysis Software. The ZrO_2 grain size distributions are plotted in Fig. 4, whereas the average grain size and monoclinic ZrO_2 phase content measured by means of XRD on polished surface is summarized in Table 6.

Grain sizes are controlled by using ultra fine powders and lowering the sintering temperature. It has been found out that the rate of tetragonal to monoclinic phase transformation increases with grain size and whereas the ageing resistance decreases [15]. The grain size of the co-precipitated and yttria-coated powder-based materials decrease with increasing yttria content. Between the yttria-coated samples with the presence of more tetragonal grains, the higher mol% of yttria content, it is clear that the finer the grain size is. Yttria-coated powder-based ceramics with a lower yttria content has larger grain size. It can be predicted that the transformation of this sample already has started during cooling after sintering and the smaller tetragonal grains have transformed into bigger monoclinic grains. The grain size distribution of yttria-coated powder-based Y-TZP materials is broader than that of yttria co-precipitated powder-based Y-TZP materials. Cubic grains correspond to the fraction of grains having a grain size above 0.8 μm which is not observed in Y-TZP ceramics although it has been reported that the larger cubic grains is the characteristic for yttria-coated powder-based ceramics even sintered at low temperature of 1,450 °C [16]. It is demonstrated in Lawson's research that yttria-coated ZrO_2 powder-based ceramics have a superior transformability combined with a better thermal degradation compared to co-precipitated powder-based materials. The inhomogeneous stabilizer distribution due to the coating technique can even result in ZrO_2 grains with a tetragonal shell around a monoclinic core [15]. Also due to low yttria diffusion rate during sintering, yttria-coated powder-based ceramics result in ZrO_2 grains with a yttria shell and a core with low yttria content [16]. It can be said that the enhanced transformability of the core structure is responsible for high high fracture toughness of coated Y-TZP materials.

ZrO_2–TiN composites with 1.75 mol% Y_2O_3 stabilizer and 0.75 wt% Al_2O_3 with different amounts of ZrO_2 and TiN were hot pressed for 1 h at 1,550 °C. An overview of the microstructures of fracture surfaces of the samples is given in Fig. 5. Three phases are observed, i.e. ZrO_2 (gray), TiN (dark) and Al_2O_3 (black). The microstructural

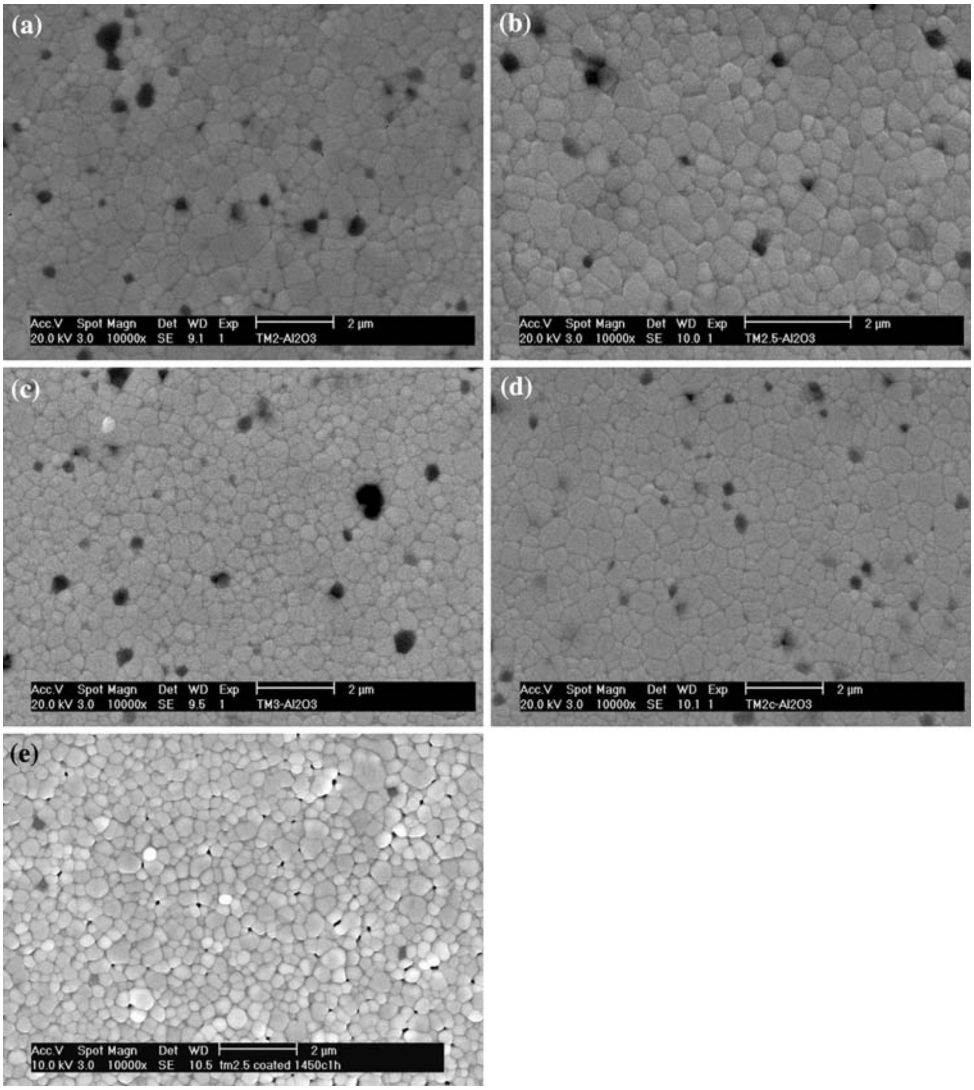


Fig. 2 SEM micrographs of TM2-SM8 (**a**), TM2.5-SM8 (**b**), TM3-SM8 (**c**), TM2-coated-SM8 (**d**) and TM2.5-coated-SM8 (**e**) on polished surface

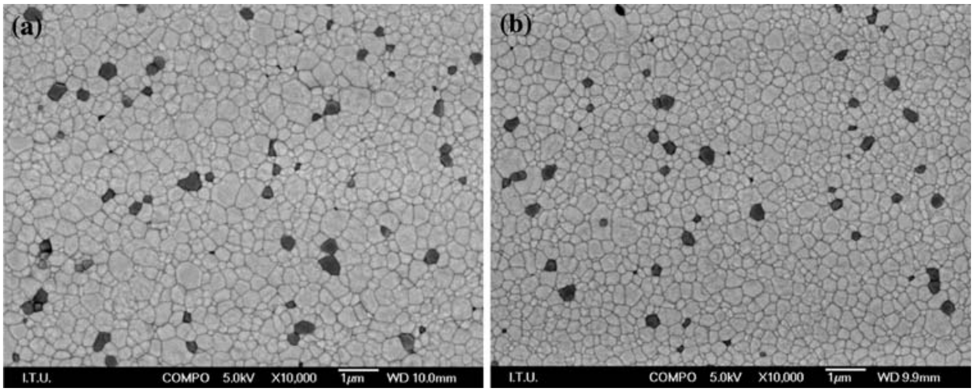


Fig. 3 SEM micrographs of TM2-Ce3 (**a**), TM3-Ce2 (**b**) on polished surface

investigation of the samples revealed that the samples were fully densified since no pores were found. Homogeneous ZrO_2–TiN microstructures are obtained, so powder mixing procedure was appropriate. 1.75 mol% yttria is sufficient enough to stabilize the tetragonal ZrO_2 phase in the ZrO_2–TiN–Al_2O_3 composites with up to 60 vol% TiN. Although this amount of yttria can be found as low for preventing transformation from tetragonal to monoclinic phase, the effect of TiN existence must be taken into consideration.

It is observed that the grains are more rounded-edged in 65/35-0.75 TM1.75-TiN sample more sharp-edged as TiN content increases from 35% to 60% sample. It has been

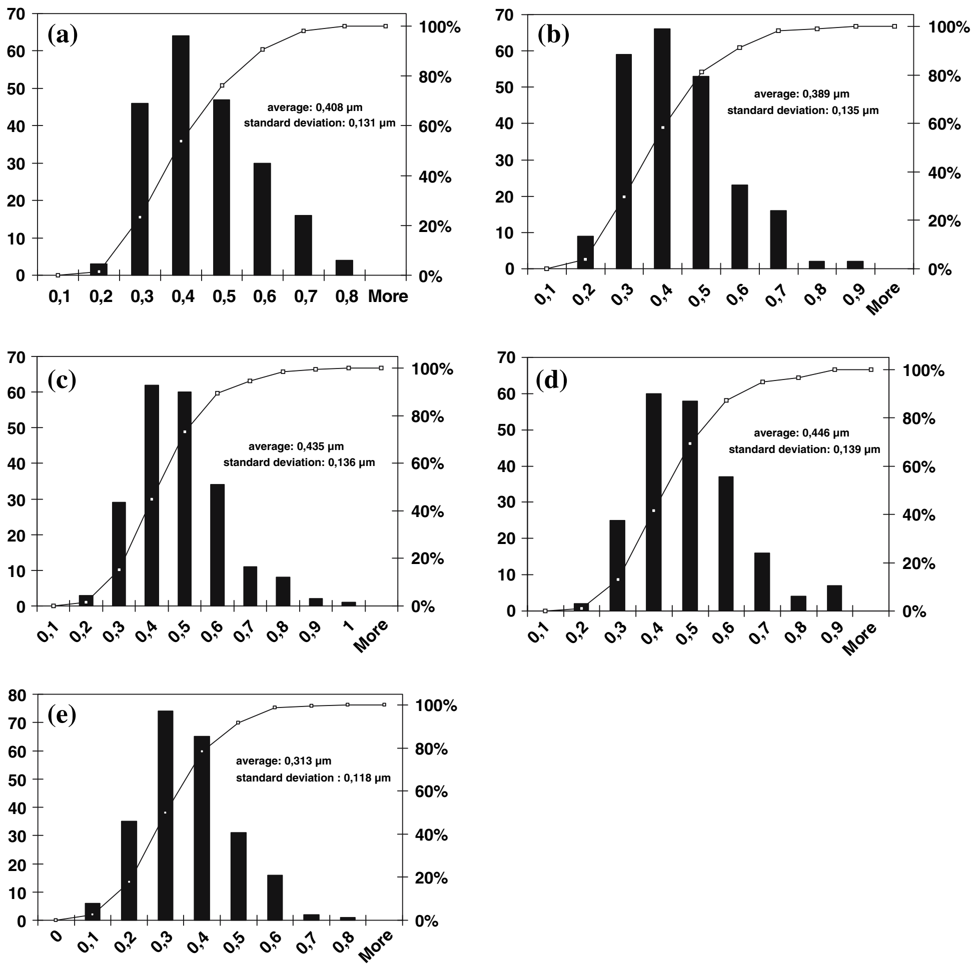


Fig. 4 Grain size distributions of the different Y-ZrO_2 ceramics: TM3-SM8 (**a**), TM 2.5-SM8 (**b**), TM 2-SM8 (**c**), TM 2-coated (**d**), TM 2.5-coated (**e**)

Table 6 Average grain size of ZrO_2 ceramic samples

Sample	Average grain size (µm)	m-ZrO_2 content (vol%)	ZrO_2 phase transformability (%)[a]
TM2-SM8	0.435 ± 0.136	0	97.46
TM2.5-SM8	0.389 ± 0.135	0	94.81
TM3-SM8	0.408 ± 0.131	0	79.92
TM2-coated-SM8	0.446 ± 0.139	3.11	90.83
TM2.5-coated-SM8	0.313 ± 0.118	1.98	81.87

[a] As determined from the m-ZrO_2 content difference measured by means of XRD on polished and fractured surfaces. The fractured surface here is the surface after the hydrothermal treatment of total 20 min

reported that the grains with rounded edges have lower stresses [17]. From the SEM micrographs of fracture surfaces of the samples it is observed that the composite with 35 vol% TiN has the smallest and the composite with 60 vol% TiN has the biggest TiN grain size which can bee seen as the dark grains. Hence, the grain size increases with increasing TiN content.

It can be observed from the SEM Micrographs in Fig. 6, that at 1,550 °C, TiN particles are bigger. It is known that TiN particles dissolve into ZrO_2 particles by increasing the sintering temperature.

Mechanical properties

The measured mechanical properties of the ZrO_2 ceramics are summarised in Table 7, revealing that the hardness is strongly influenced by the addition of Al_2O_3, the Y_2O_3 stabilizer content and the processing route. The E modulus is hardly influenced by the addition of 2 wt% Al_2O_3 or the amount of stabilizer.

For yttria co-precipitated powder-based Y-TZP materials, as yttria content increases hardness increases. Yttria-coated samples have an inhomogeneous stabilizer distribution and

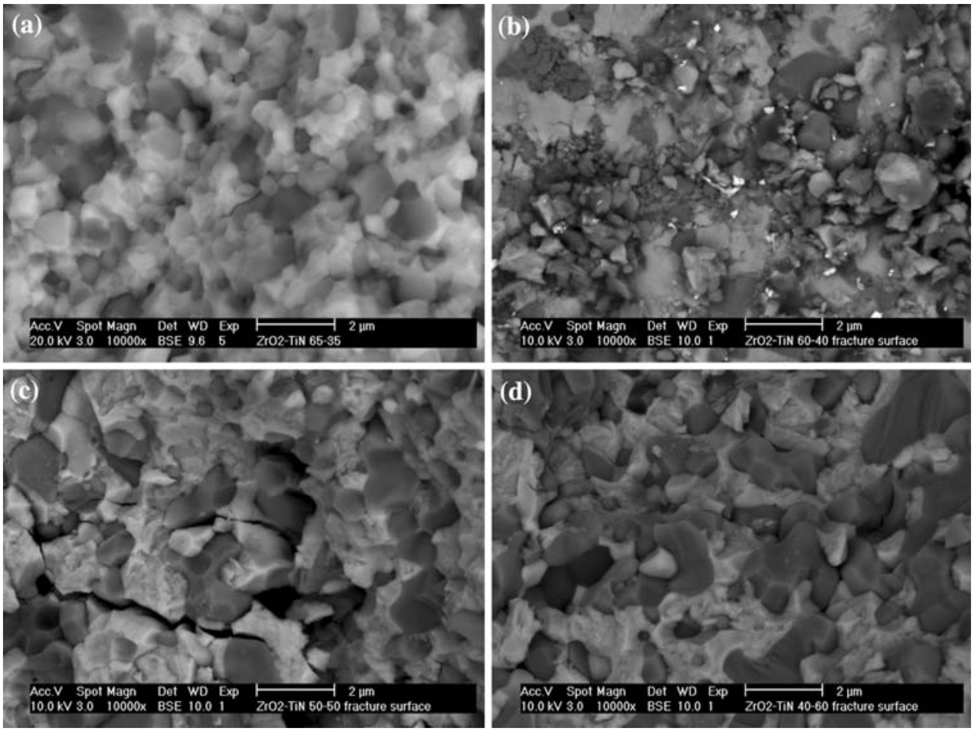


Fig. 5 SEM micrographs of 65/35-0.75 TM1.75-TiN (**a**), 60/40-0.75 TM1.75-TiN (**b**), 50/50-0.75 TM1.75-TiN (**c**), 40/60-0.75 TM1.75-TiN (**d**) on fracture surface

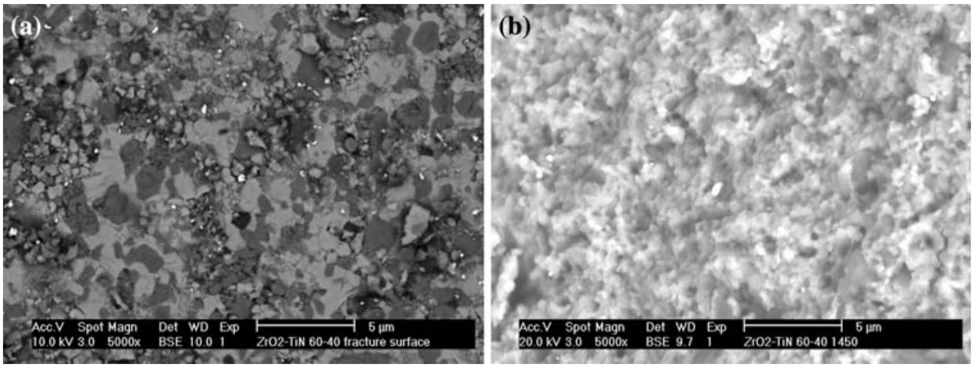


Fig. 6 SEM Micrographs of 60/40-0.75 TM1.75-TiN-1 h at 1,550 °C (**a**), 60/40-0.75 TM1.75-TiN-1 h at 1,450 °C (**b**) on fracture surface

Table 7 Mechanical properties of Y-TZP and Y-Ce-TZP materials

Material grade	Density (g/cm^3)	Vickers hardness (kg/mm^2)	Young's modulus (GPa)
TM2-SM8	5.99	1,250 ± 4	207
TM2.5-SM8	5.97	1,315 ± 10	211
TM3-SM8	5.97	1,342 ± 11	209
TM2-coated-SM8	6.01	1,301 ± 9	207
TM2.5-coated-SM8	6.05	1,341 ± 25	210
TM3-Ce2-SM8	6.30	1,379 ± 21	–
TM2-Ce3-SM8	5.84	1,253 ± 6	–

existence of ZrO_2 grains with a highly transformable tetragonal shell around a monoclinic core [9]. The Regarding the yttria-coated starting powder-based ceramics, the table shows that the TM2-coated-SM8 sample shows acceptable hardness, whereas the TM2.5-coated-SM8 sample shows a higher hardness. Exactly the same trend is observed with respect of the yttria content for the mixed powder-based ceramics. This clearly proves that an overall yttria content of 2.5 mol% would be preferred when a higher hardness is targeted.

Although it is known that the hardness slightly increases with increasing CeO_2 content [14], the role of yttria is more dominant in Y-Ce-TZP materials whereas higher yttria content powder-based Y-Ce-TZP materials have higher

Table 8 Mechanical properties of 1.75 mol% Y_2O_3-stabilised ZrO_2–TiN composites with varying TiN content and 0.75 wt% Al_2O_3 [13]

TiN content (vol%)	ρ (g/cm^3)	HV_{10} (GPa)	K_{IC} (Mpa m$^{1/2}$)	E (GPa)
35	5.85	13.75 ± 0.08	7.1 ± 0.2	261 ± 10
40	5.81	13.65 ± 0.09	5.9 ± 0.1	290 ± 7
50	5.69	13.49 ± 0.26	6.3 ± 0.5	319 ± 5
60	5.60	13.55 ± 0.25	5.0 ± 0.3	344 ± 8

hardness. It can be concluded that 2–3 mol% CeO_2 addition is not effective on the hardness of Y-Ce-TZP materials in the presence of same mol% yttria.

The ZrO_2–TiN composite samples have been prepared and tested for mechanical properties before in MTM laboratories for a previous study [13], and the data is as in Table 8.

For the sample hot pressed at 1,550 °C, the mechanical properties are lower than the sample hot pressed at 1,450 °C, however, the hydrothermal stability has increased. The general trend can be increasing the hot-press temperature decreases the mechanical properties of the zirconia composites. Since the yttria content and Al_2O_3 content is same for all the samples, it is observed that the hardness of the composites decreases with decreasing ZrO_2 content. The decreasing of hardness can be the result of TiN grain size increasing with TiN content. It is very clear from the tables that the Elastic Modulus increases by decreasing the ZrO_2 content and increasing the TiN content.

The fracture toughness decreases by increasing the TiN content so increasing TiN grain size. The reason for this could be the lower thermal coefficient of TiN ($\alpha_{0-1,000\,°C} = 9.4 \times 10^{-6}$/C)^{16} compared to yttria-stabilized ZrO_2 ($\alpha_{0-1,000\,°C} = 10 \times 10^{-6}$/C)^{14} causing compressive residual stresses on TiN phase [13]. This residual stress can provide an extra fracture-toughening mechanism on TiN.

Table 9 shows the frictional behaviour of different grades of powder-based Y-TZP, Y-Ce-TZP and ZrO_2–TiN composite materials when fretted against Alumina ball under a load of 5 N for 10,000 cycles under joint synovial simulated liquid as lubricant. It is known from the literatures that the average coefficient of friction is strongly related to the average grain size [8]. It has been found that COF increases with increasing grain size. However, for Y-TZP samples, it is observed that the grade with the smaller grain size which is TM3-SM8, has higher coefficient of friction. For Y-Ce-TZP and composite samples, the outcome of the study [8] is effective whereas the grain size increasing COF is increasing.

In the previous studies [8] it has been found that as the tetragonal grain size increases, volumetric wear loss on the sample increases, which can be said for the composite samples; it is clear that as grain size increases with TiN content, COF increases and wear on ball and sample increases. Wear on the other samples is so low that it's not possible to calculate.

Volumetric wear loss on the counterbody (alumina ball) increases with the high surface roughness like in 3Y2Ce material. For the composite samples, the volumetric wear loss on the sample increases as the fracture toughness increases. In order to use Y-TZP, Y-Ce-TZP and ZrO_2–TiN composite materials successfully in the applications of femoral heads for hip prosthesis where tribological properties are important, a compromise between the fracture toughness and wear resistance needs to be obtained.

The morphology of wear on the fretted surfaces of different grades of Y-TZP, Y-Ce-TZP and composite samples are shown in Fig. 7. Abrasive scratches parallel to the fretting direction are present both on counterbody and sample surfaces. The compositional analysis of the transfer layer on the surfaces shows Al_2O_3 presence which can show material transfer from the counterbody. Very small microcracks are observed on the sample surfaces that are not necessary to take into consideration, especially on the

Table 9 Wear properties of Y-TZP, Y-Ce-TZP materials and 1.75 mol% Y_2O_3-stabilised ZrO_2–TiN composites

Material	Surface roughness Ra (nm)	Volumetric wear loss on sample (μm3)	Max. depth on sample (μm)	Volumetric wear loss on alumina ball (μm^3)	Coefficient of friction
TM2-coated	16.6×10^{-3}	Just scratches	~0.03	47×10^3	0.468 ± 0.11
TM3-SM8	14.23×10^{-3}	Just scratches	~0.09	38×10^3	0.508 ± 0.083
2Y3Ce	79.91×10^{-3}	Just scratches	~0.16	43×10^3	0.438 ± 0.049
3Y2Ce	119.77×10^{-3}	Just scratches	~0.25	58×10^3	0.396 ± 0.105
60/40-0.75 TM1.75-TiN	192.75×10^{-3}	6.5×10^4	~0.47	28×10^3	0.515 ± 0.053
50/50-0.75 TM1.75-TiN	252.37×10^{-3}	22×10^4	~0.9	37×10^3	0.624 ± 0.069

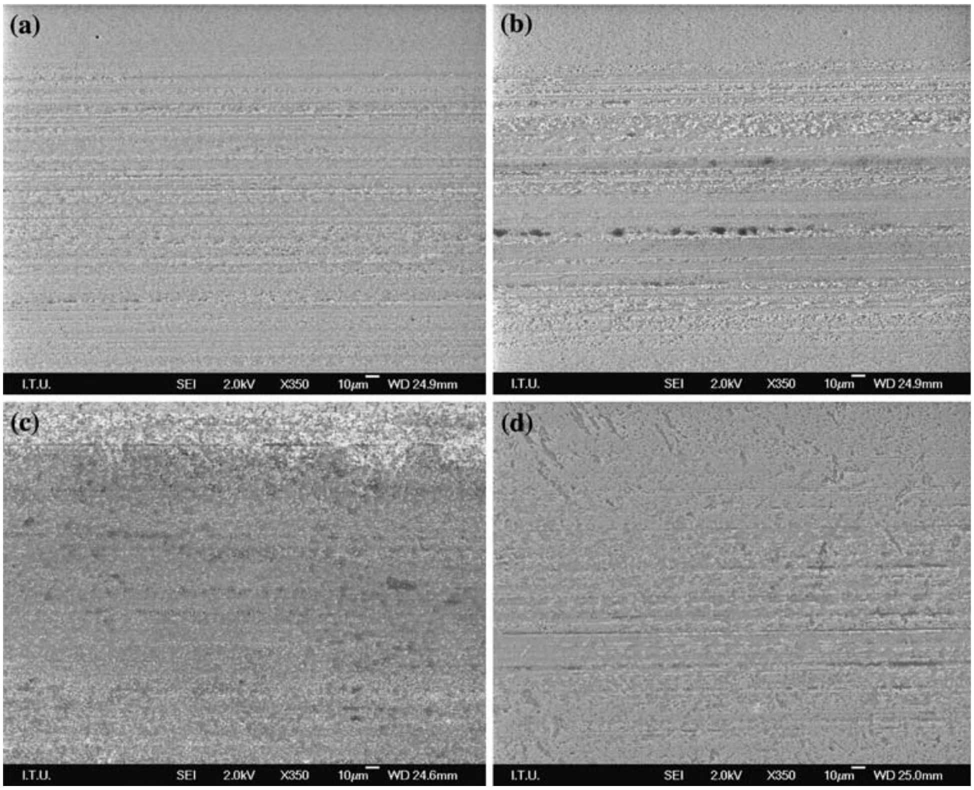


Fig. 7 SEM micrographs showing the morphology of wear on the fretted surfaces of TM2 Coated (**a**), TM3-SM8 (**b**), 50/50-0.75 TM1.75-TiN (**c**), 2Y3Ce (**d**)

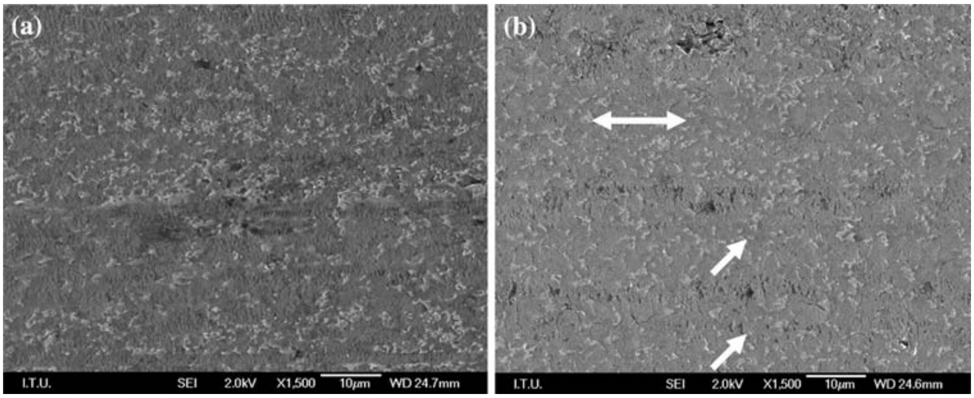


Fig. 8 SEM micrographs showing the direction of micro-cracking patterns on the fretted surfaces of 60/40-0.75 TM1.75-TiN (**a**), 50/50-0.75 TM1.75-TiN (**b**) Double pointed arrow indicates the fretting direction and one point arrow indicates the micro-crackings.

composite surfaces as shown in Fig. 8. The patterns of micro-cracking can be observed as perpendicular to the sliding direction, as shown in Fig. 8. A different morphology of the worn tracks on the surface of 3Y-2Ce material is dependent on the surface roughness which is very high for this sample.

It is known from the literatures that during the fretting wear process, t-ZrO_2 to m-ZrO_2 transformation-induced by thermal or mechanical stresses, such as repeated cycling, occurs [8]. The presence of lubricant may increase the speed of transformability.

XRD analysis and hydrothermal stability

XRD analysis of the polished flat samples revealed that except for TM-coated ones, all investigated Y-TZP and Y-Ce-TZP samples remain fully tetragonal after sintering for 1 h at 1,450 °C as shown in Fig. 9. A very small amount of monoclinic zirconia phase was found in the powder mixtures TM2-coated and TM2.5-coated.

The hydrothermal degradation of the Y-TZP and composite ceramic grades is examined after 5, 10 and 20 min at 200 °C by means of a consecutive thermal cycle of 5, 5 and

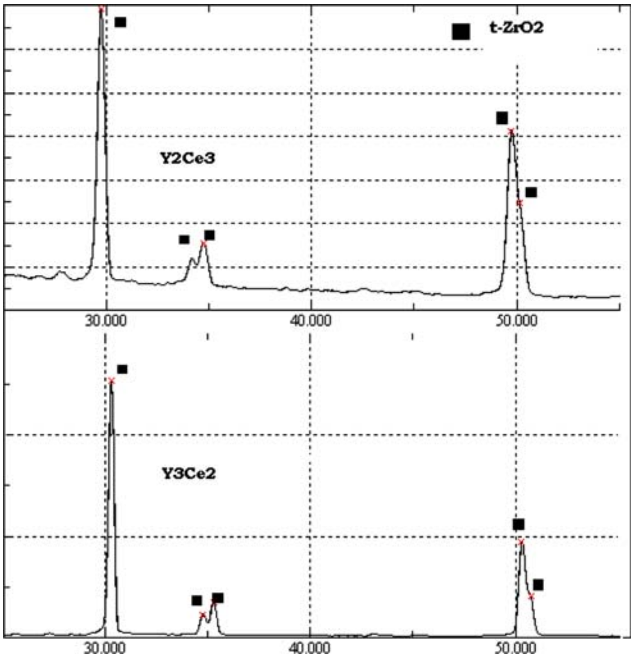


Fig. 9 XRD analysis showing the tetragonal phase peaks of Y-Ce-TZP samples

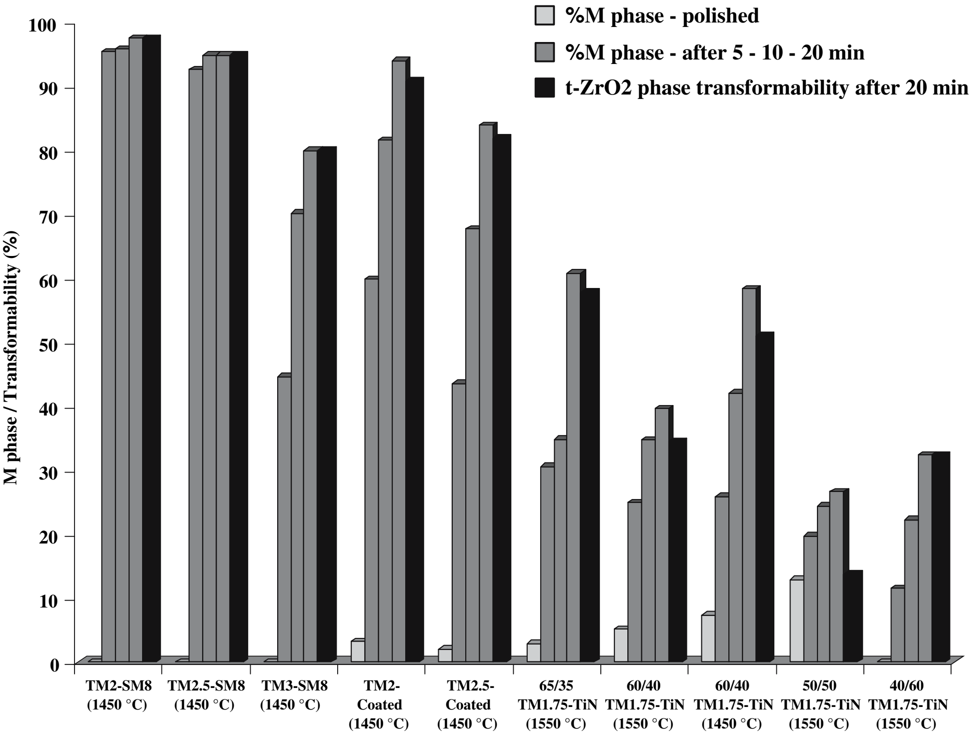
10 min. The Thermal cycle was interrupted after 5 min. The starting materials were rectangular bars polished on both sides. The amount of monoclinic ZrO_2 was measured by XRD on both polished sides of the samples. The reported value is the average from both sides. The monoclinic phase is the result of tetragonal to monoclinic phase transformation due to the thermal treatment. ZrO_2 phase transformability is defined as the difference in the percentage of monoclinic and tetragonal zirconia phase obtained from XRD patterns of polished and fractured surfaces after totally 20 min hydrothermal treatment. The transformation of the tetragonal to monoclinic phase causes a volume expansion accompanied by microcracks and material spallation at the surface. It is known that the grain size of the tetragonal phase in Y-TZP ceramics strongly controls the transformability [1].

The amounts of measured m-ZrO_2 as function of the thermal treatment time is summarised, allowing to calculate the amount of transformed t-ZrO_2 phase as function of the thermal annealing, which is graphically presented in Fig. 10.

All zirconia grades already substantially transform during the first 5 min of ageing in steam at 200 °C.

The coated powder-based grades have a higher thermal degradation resistance, despite the small amount of monoclinic ZrO_2 phase content after hot-pressing for 1 h at 1,450 °C, compared to the powder mixed grades. For both processing routes, the degradation resistance increases with increasing overall yttria content. One of the important factors in ageing is the critical tetragonal grain size that is yttria content dependent. From literatures it is known that there is a certain critical value for tetragonal phase retention and when the grain size exceeds that value, the tetragonal crystals with a larger grain size spontaneously transform to monoclinic ZrO_2 during cooling [17]. Only a small amount of m-ZrO_2 is measured for the TM2-coated-SM8 and TM2.5-coated-SM8 grades.

Fig. 10 The amount of measured m-ZrO_2 and t-ZrO_2 phase transformability as function of the thermal annealing



During hydrothermal testing however, yttria is leached out of the ceramic components which will result in a reduced yttria content which will induce spontaneous transformation of the reduced yttia stabiliser content t-ZrO_2 crystals. In order to prevent this degradation, the critical grain size must be smaller than the critical grain size for a uniform yttrium distribution. It has been reported that when the yttria content increases the critical grain size for spontaneous transformation also increases and an increasing yttria content results in more cubic phase ZrO_2 grains that are not susceptible to transformation [17].

It has also been reported that the increase of yttria content (2–4 mol%) does not necessarily result in an increase in phase stability [15]. However from the obtained experimental data, it can be observed that the increasing mol% of yttria decreases the t-ZrO_2 transformability and improves the resistance against hydrothermal degradation of the mixed as well as coated ZrO_2 ceramic samples.

Among all Y-TZP ceramic samples and the ZrO_2–TiN ceramic composites, composites with high vol% TiN content have less transformed. The lowest t-ZrO_2 transforming composites are with 50 vol% TiN.

As observed from Fig. 10, generally, as the TiN content increases, the transformability decreases. The tensile stresses generated in the ZrO_2 matrix are assumed to increase the transformability of the t-ZrO_2 phase and the composite transformability observed from the graph as the higher the amount of ZrO_2, the higher the transformability. It is observed in mechanical properties that the toughness increases by decreasing TiN content, so it is valid for composite samples that the transformation zone acts as preventing the crack propagation enhancing the fracture toughness. The presence of monoclinic phase before the treatment is thought as the source of high fracture toughness due to transformability of metastable tetragonal zirconia grains. Also lower thermal coefficient of TiN ($\alpha_{0-1,000\ °C} = 9.4 \times 10^{-6}$/C)[16]) compared to yttria stabilized ZrO_2 ($\alpha_{0-1,000\ °C} = 10 \times 10^{-6}$/C)[14] will cause compressive residual stresses on TiN phase. It is significant that the grain size increases by the increasing of TiN content as well as m-ZrO_2 content and t-ZrO_2 transformation % decreases. The samples that have higher TiN content have no monoclinic ZrO_2 phase content after hot-pressed 1 h at 1,550 °C. For the composite samples that contain no monoclinic ZrO_2 phase as measured on the polished surfaces, the ZrO_2 phase transformability is equal to the measured monoclinic content on the fracture surfaces which are measured after the 20 min of hydrothermal treatment.

Among the composites 40 vol% TiN containing composites, the sintering temperature is changed between 1,450 °C and 1,550 °C. Although it is known that the mechanical properties decrease as the sintering temperature increases, for hydrothermal behaviour this characteristic is effective. After the second cycle of 10 min. treatment, the monoclinic ZrO_2 content so the tetragonal ZrO_2 transformability has increased highly for the composite sample hot-pressed at 1,450 °C according to the other samples hot-pressed at 1,550 °C. It can be explained as TiN particles dissolving into ZrO_2 particles by increasing the sintering temperature.

Conclusion

The transformation of yttria and ceria stabilized zirconia ceramics and composites from t-ZrO_2 to m-ZrO_2, is influenced by the powder processing techniques, grain size, yttria content and distribution etc. Low yttria containing tetragonal grains are very susceptible to transformation under thermal stress (hydrothermal treatment) conditions.

For both yttria coating and co-precipitated techniques, the hardness decreases when decreasing the overall yttria content from 2.5 mol% to 2.0 mol% whereas the ZrO_2 grain size hardly changed. Hydrothermal testing however revealed that the stability of the yttria-coated powder-based grades is higher than that obtained by powder mixing.

Hardness of Y-Ce-TZP samples were not influenced by CeO_2 addition. Lower amounts of CeO_2 addition was insufficient to change the mechanical properties.

The hardness and fracture toughness was found to decrease almost linearly with increasing TiN content from respectively 1,375 kg/mm^2 and 7.1 Mpa m$^{1/2}$ for the 35 vol% TiN composite down to 1,355 kg/mm^2 and 5.0 MPa m$^{1/2}$ for the 60 vol% TiN composite, due to the larger TiN grain size in the composite samples with the higher TiN contents. Since TiN is more brittle, the fracture toughness decreases with increasing TiN content. Since the fracture toughness decreases linearly with the transformability, transformation toughening mechanism was attributed as playing a major in the enhancement of toughness of ZrO_2–TiN composites.

The wear mechanism for Y-TZP Y-Ce-TZP ceramics and ZrO_2–TiN composites is slight abrasion. Generally wear volume increases with the grain size and this can be related to increased transformability of t-ZrO_2 containing large tetragonal grains. Other microstructural variables, such as yttria content and distribution, surface roughness are the important influential factors in the fretting wear of Y-TZP Y-Ce-TZP ceramics and ZrO_2–TiN composites. The presence of lubricant as used between the femoral head in hip prosthesis, may influence as decreasing wear and increasing transformability resulting in enhanced fracture toughness.

The hydrothermal stability of the ZrO_2–TiN composites, however, increases linearly with increasing TiN content. It is possible that, with increasing TiN content, a smaller volume fraction of t-ZrO_2 grains becomes susceptible to hydrothermal transformation due to the shielding effect of the present TiN grains. Therefore, a decreasing mechanical transformability might be an indicator of an increasing hydrothermal stability. The reduction in toughness and hardness, which decrease linearly, is parallel to the decrease of transformation toughening. Hence, reduction in hardness and toughness because of TiN grain size increasing, decreases the monoclinic ZrO_2 content so the tetragonal ZrO_2 transformation after the hydrothermal treatment of total 20 min at 200 °C.

Among all samples, the lowest t-ZrO_2 transforming is achieved in ZrO_2–TiN composites with addition of 1.75 mol% yttria as co-precipitated and 0.75 wt% Al_2O_3 and containing 50 vol% TiN, sintered 1 h. at 1,550 °C. Increasing yttria content of the composite can decrease, and increasing the Al_2O_3 content can increase the toughness.

Acknowledgements M. Arin would like to thank International Coordination of Istanbul Technical University and Kathoieke Univesiteit Leuven for giving an opportunity to study in the framework of Erasmus exchange programme. M. Arin also thanks to the laboratory technician H. H. Sezer and Research Assistant V. Ezirmik in Istanbul Technical University.

References

1. Gremillard L, Chevalier J, Epicier T, Fantozzi G (2002) J Am Ceram Soc 85(2):401
2. Basu B, Vleugels J, Biest OV (2004) Mater Sci Eng A366:338
3. Mudali UK, Sridhar TM, Raj B (2003) Sadhana 28:601
4. Hannink RHJ, Swain MV (1994) Annu Rev Mater Sci 24:359
5. Chevalier J, Cales B, Drouin JM (1999) J Am Ceram Soc 82(8):2150
6. Fang P, Gu H, Wang P, Landuyt JV, Vleugels J, Biest OV (2005) J Am Ceram Soc 88:1929
7. Vleugels J, Zhao C, Biest OV (2005) Mater Sci Forum 492–493:699
8. Basu B, Vleugels J, Biest OV (2004) J Eur Ceram Soc 24:2031
9. Vleugels J, Yuan ZX, Biest OV (2002) J Eur Ceram Soc 22:873
10. Chevalier J (2006) Biomaterials 27:535
11. Hraguchi K et al (2001) J Bone Joint Surg 83-B:996
12. Vleugels J, Biest OV (1999) J Am Ceram Soc 82(10):2717
13. Salehi S, Biest OV, Vleugels J (2005) J Eur Ceram Soc 5873:1
14. Huang SG, Vleugels J, Li L, Biest OV, Wang PL (2005) J Eur Ceram Soc 25:3109
15. Lawson S, Gill C, Smith GP, Egerton TA, Mccolgan P (1993) Third Euro-Ceramics V.3:507
16. Singh R, Gill C, Lawson S, Dransfield GP (1996) J Mater Sci 31:6055
17. Lawson S (1995) J Eur Ceram Soc 15:485