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New Y-TZP powders for medical grade zirconia

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There is interest in using zirconia for biomedical applications as ball heads for total hip prostheses. Two potential types are under discussion: partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZP) materials. Because of its enhanced material properties, TZP stabilized with yttria is favourable. To eliminate high amounts of natural radioactive impurities, the precursors are purified. The kind of precursor and purification method determine the powder impurity level. The disadvantage of Y-TZP is that the hydrothermal decomposition reaction method is that it depends very strongly on the grain size and the distribution of the stabilizing yttria within the zirconia grains. Thermodynamical and kinetic investigations on high purity coprecipitated and yttria-coated zirconia powders show different behaviours. Y-TZP materials based on yttria-coated zirconia powders show excellent mechanical strength of more than 1000 MPa, a Weibull modulus of up to 20 and a fracture toughness of 9 MPa$\sqrt{m}$. The material properties of Y-TZP ceramics based on coprecipitated powders and prepared under the same conditions are less attractive. It is expected that materials based on yttria-coated zirconia will show enhanced properties compared to materials derived from coprecipitated powders. Therefore Y-TZP materials derived from yttria-coated powders are very attractive as medical grade zirconia.

1. Introduction

Partially stabilized zirconia was introduced to the orthopedic community a few years ago because of its attractive mechanical properties. It seems that partially stabilized zirconias are suitable and safe materials for femoral ball heads of THR-systems [1, 2]. The so-called PSZ-grades, which consist of cubic matrix grains having tetragonal precipitates within those grains, are of less interest because of their relatively high porosity of about 4%. Furthermore PSZ-ceramics are normally based on powders having significant amounts of radioactive and chemical impurities [3]. More attractive zirconia ceramics being used in biomedical applications are TZP-ceramics, usually stabilized by yttria. The microstructure of Y-TZP is very fine grained and the densities reach nearly theoretical values. To achieve such results, the powders used for the fabrication of Y-TZP ceramics, must be fine grained and have a very high chemical purity. In order to qualify the zirconia powders for the fabrication of hip joints, their radioactive impurities have to be minimized by purification of the precursors, because the radioactive impurities form solid solutions with the zirconia and show a similar chemical behaviour to the zirconia itself.

Typical purification methods are distillation, sublimation or solvent extraction, but chromatographic or ion-exchange extraction processes are also of interest. The selection of the purification route depends on the chemical precursor selected. This means that for the purification of $ZrCl_4$ a distillation process is preferably applied, because $ZrCl_4$ is a liquid and can be distilled off from impurities very easily. If $ZrOCl_2$ or $ZrO(NO_3)_2$ are used as precursors, a different purification method, such as chromatographic extraction, has to be used.

After the purification process of the chemical zirconium salts is finished, normally a precipitation process follows and finally the precipitated powder is calcined. During the precipitation process the size of the precipitates is controlled in order to achieve very fine grained crystallites 50–250 nm in size after calcination.

For the production of Y-TZP ceramics, the yttria has to be distributed very homogeneously in the zirconia matrix. The most common method to realize this is a coprecipitation process: the stabilizing amount of yttria is added to the solution of purified zirconium salt as an yttrium salt before the precipitation and calcination process is started [4]. There exists another approach to introduce yttria: a coating of already calcined zirconia particles [5]. By using such a powder, the formation of tetragonal phase is achieved during sintering. It has to be determined whether or

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not a Y-TZP ceramic based on yttria coated powder leads to the excellent material properties shown by commercially available Y-TZP ceramics.

2. Experimental procedures

As a reference a powder (powder 1) without yttria was used for the powder investigations. Two commercially available coprecipitated powders containing 5.2 wt % of yttria (powder 3 and 4) and a zirconia powder coated with 4.8 wt % of yttria (powder 2) were prepared by the following steps:

- milling in an attrition mill containing Y-TZP milling media and Y-TZP discs
- addition of an organic binder system; optimized for yttria-coated powder; identical for all powders
- spray drying in the NIRO laboratory atomizer 'HI-TEC'

The powder preparation was assisted by chemical measurements to control any contamination. The measurements were done in the SIEMENS spectrometer SRS300. In order to analyse the phase transformation from monoclinic to tetragonal a SIEMENS diffractometer D500 with a PAAR chamber was used. For the investigation the reflections [1 1-1] ($2\theta = 28.4°$) and [1 1 1] ($2\theta = 31.6°$) of the monoclinic phase and the [1 1 1]-reflection ($2\theta = 30.3°$) of the tetragonal phase were analysed.

Test bars of the ready-to-press powders were formed by uniaxial pressing, followed by sintering in an electrically heated furnace from NABER.

For material characterization, the test bars were prepared according to the German draft standard DIN 51110 (4-point-method). For the evaluation of fracture toughness, the notched beam technique was used. Testing was done in ZWICK 1435 equipment.

3. Results

Tables I and II show the results of chemical analysis before and after powder preparation. No significant difference in chemical purity between the starting powders and the ready-to-press powders is found. All data are within the confidence intervals of the measurements. Powder 4 had the highest chemical purity, followed by powder 2. Significant amounts of impurities were detected in powder 3 (Al_2O_3, SiO_2, TiO_2 and CaO).

X-ray investigations showed a big difference in the amount of tetragonal phase in the starting powders. Table III summarizes the results. As can be seen, the amount of tetragonal phase in the coprecipitated powders (3 and 4) is quite high, while in the coated powder 2 more than 90% of the particles remain monoclinic.

Since the starting powders showed different amounts of tetragonal phase, it was expected that the monoclinic → tetragonal phase transformation would be different in the different powders. Fig. 1–4 show the phase transformation behaviour of the different powders. In powder 4 phase transformation is already complete at 800 °C. Further heating leads to a higher peak intensity due to the crystallization effect.

TABLE I Chemical impurities of the Y-TZP powders

	Impurity content (wt %)		
Impurity	powder 2	powder 3	powder 4
Na_2O	< 0.05	< 0.05	< 0.05
K_2O	0.01	0.01	0.01
MgO	< 0.1	< 0.1	< 0.1
CaO	< 0.01	0.03	0.01
Al_2O_3	0.1	0.28	< 0.05
SiO_2	< 0.03	0.11	< 0.03
TiO_2	0.01	0.11	0.02
Fe_2O_3	0.01	< 0.01	< 0.01
HfO_2	1.96	1.78	1.67
Y_2O_3	4.8	5.2	5.2

TABLE II Chemical impurities of the ready to press powders

	Impurity content (wt %)		
Impurity	powder 2	powder 3	powder 4
Na_2O	< 0.05	< 0.05	< 0.05
K_2O	0.01	0.01	0.01
MgO	< 0.1	< 0.1	< 0.1
CaO	< 0.01	0.03	< 0.01
Al_2O_3	0.1	0.26	< 0.05
SiO_2	< 0.03	0.1	< 0.03
TiO_2	0.01	0.1	0.01
Fe_2O_3	< 0.01	< 0.01	< 0.01
HfO_2	1.95	1.68	1.84
Y_2O_3	4.8	5.2	5.2

TABLE III Phase composition of the Y-TZP powders

Powder	Monoclinic (%)	Tetragonal (%)
2	92	8
3	27	73
4	27	73

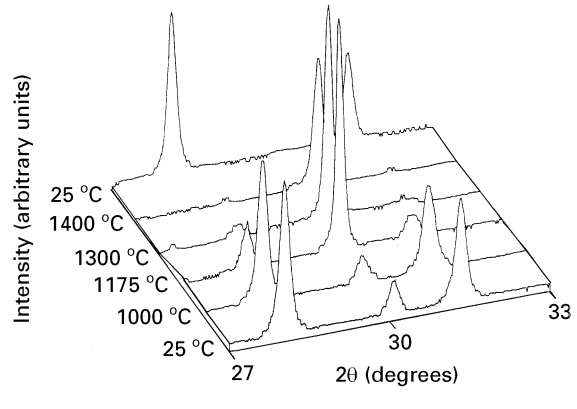

Figure 1 Phase transformation in unstabilized zirconia powder.

With cooling down after treatment at 1400 °C, no monoclinic phase appears. The tetragonal phase remains stable. In the coprecipitated powder 3, forming of the tetragonal phase is completed at about 1000 °C. Despite of this difference, the behaviour is similar to powder 4. Powder 4 has a specific surface area of 14 m^2/g after powder preparation, and powder 3 only 9 m^2/g. This corresponds to the specific surface areas of the starting powders.

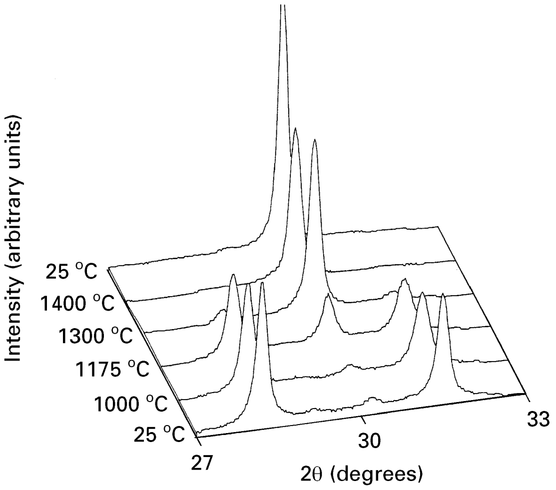

Figure 2 Phase transformation in yttria-coated powder 2.

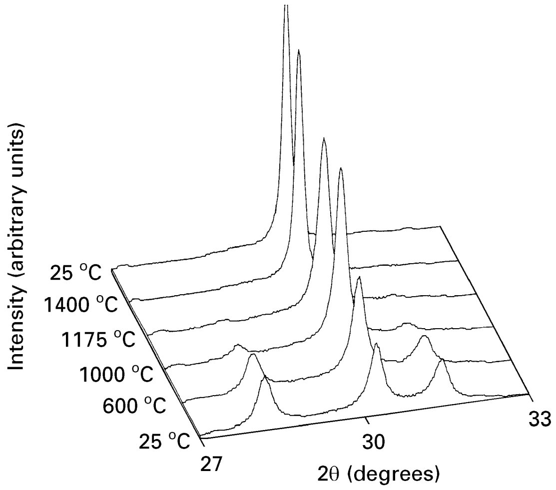

Figure 3 Phase transformation in coprecipitated powder 3.

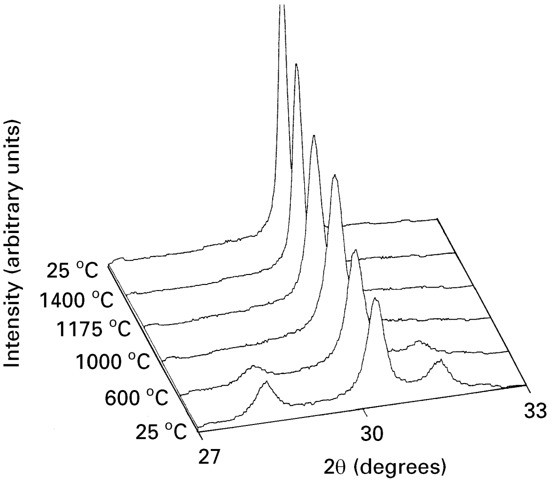

Figure 4 Phase transformation in coprecipitated powder 4.

The specific surface area of powder 2 after preparation was 13.5 m^2/g, but the behaviour of the phase transformation monoclinic → tetragonal was quite different from powder 4. Upto the well-known transformation temperature of about 1175 °C no remarkable intensity of the [111]-reflection of the tetragonal phase was formed. From that temperature, a remarkable increase in the intensity of the tetragonal phase coupled with a decrease in the intensity of the monoclinic phase was detected. Although the intensity of the monoclinic phase decreased steadily, at 1300 °C a small monoclinic peak could still be detected. The phase transformation monoclinic → tetragonal was completed at 1400 °C. As in powder 3 and 4 already described, no retransformation tetragonal → monoclinic was detected.

The unstabilized powder 1, which was produced under the same conditions as the yttria-coated powder, showed a different behaviour during high temperature X-ray investigations. As is demonstrated in Fig. 1, the phase transformation from monoclinic to tetragonal takes place at 1175 °C. The intensity of the tetragonal [1 1 1] reflection is significantly higher than it is in the yttria-coated powder at the same temperature. In the unstabilized powder the phase transformation to tetragonal is nearly completed. By cooling down, the expected retransformation to the monoclinic modification takes place.

Sintering trials have demonstrated that parts made from powder 2 lead to higher densities than those made from the coprecipitated powders prepared under identical conditions. The densities of sintered materials (material 2 is made from powder 2, etc.) which were uniaxially pressed at 200 MPa and afterwards sintered at different temperatures are shown in Fig. 5. It is evident that the final density of ceramic parts made from the coated powder is higher than that of parts made from the coprecipitated powders. At 1500 °C the achievable density of powders 3 and 4 is less than in powder 2. If, when forming green parts, a higher pressure is applied, the green density becomes higher. With respect to the final density no significant benefits in powder 2 are seen, but the final density of powder 3 and 4 is increased. Fig. 6 demonstrates the influence of the pressure on the green and final densities for materials sintered at 1430 °C. Material 3 has similar green densities to material 2, but the final density is significantly lower and comparable with the densities of material 4, although the green densities are lower in material 4.

As is known, sintering of coprecipitated ready-to-press powders at temperatures higher than 1450 °C leads to discontinuous grain growth. In Fig. 7 the microstructure of material 3 sintered at 1500 °C is shown. From this figure it can be seen that the grain size of the tetragonal zirconia grains is about 1 μm or even less, but exaggerated grain growth leading to grains bigger than 5 μm is detected. After reduction of the sintering temperature to 1450 °C material 3 still shows grains of size 1 μm as well as grains of a size smaller than 0.5 μm (Fig. 8). In material 4 this effect cannot be seen. At a sintering temperature of 1450 °C the microstructure is very homogeneous (Fig. 9) and the grains are smaller than 0.5 μm. The microstructure of material 2 prepared from powder 2 and sintered at 1450 °C shows an identical microstructure to material 4. Due to the high sintering activity the temperature can be reduced further to 1410 °C. This leads to an extremely fine-grained microstructure as demonstrated in Fig. 10. The grain size is about 0.2–0.3 μm.

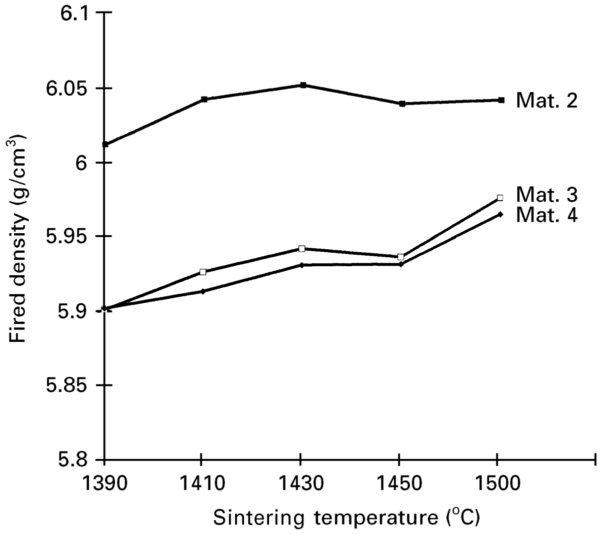

Figure 5 Density of sintered samples at different temperatures: ■ material 2; material 3; ◆ material 4.

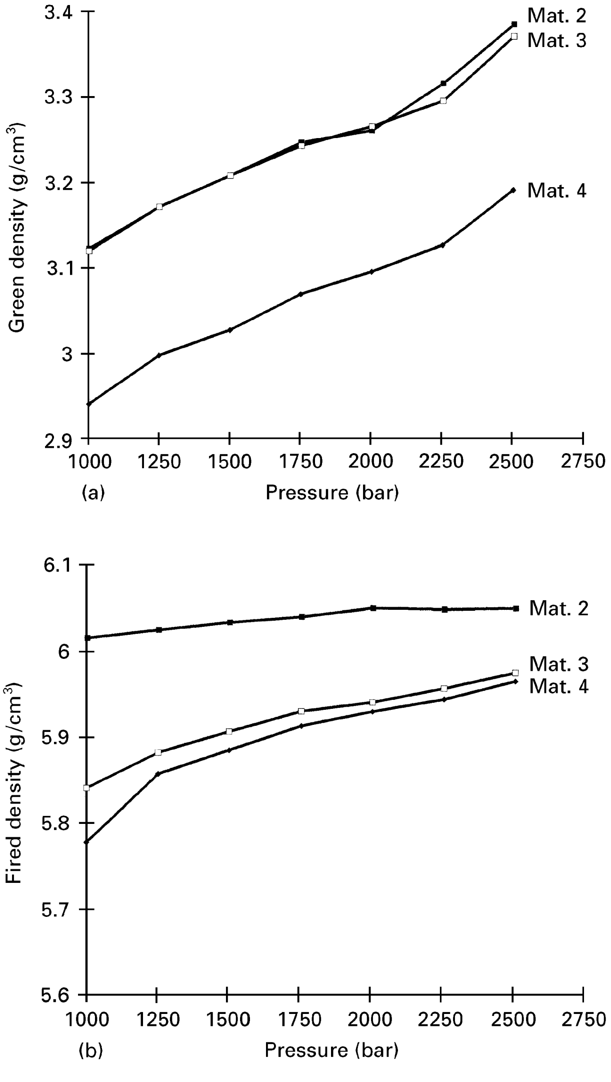

Figure 6 Influence of the applied pressure on (a) green densities and (b) fired densities for samples sintered at 1430 °C: ■ material 2; □ material 3; ◆ material 4.

The mechanical properties of the materials differ significantly. The data are summarized in Table IV. Material 2 shows the highest values followed by material 3, with material 4 having the lowest values. The

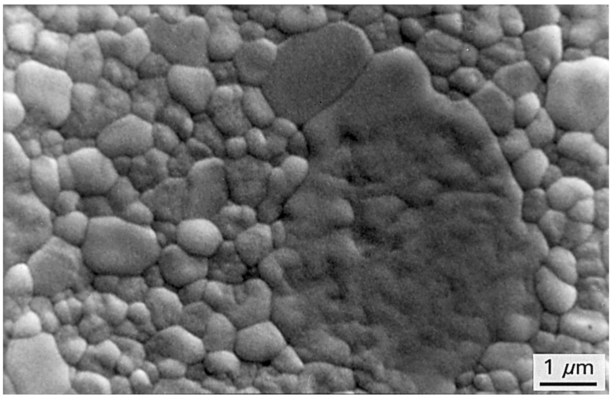

Figure 7 Microstructure of material 3 after sintering at 1500 °C.

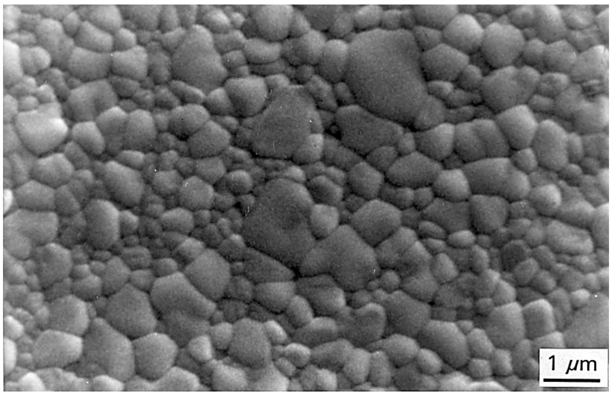

Figure 8 Microstructure of material 3 after sintering at 1450 °C.

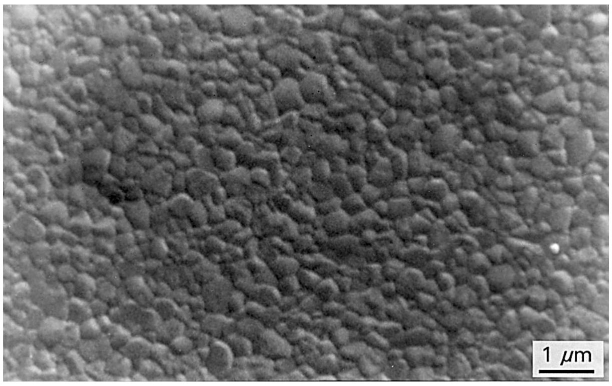

Figure 9 Microstructure of material 4 after sintering at 1450 °C.

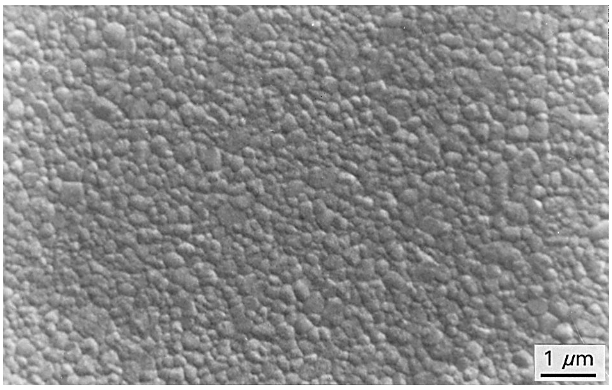

Figure 10 Microstructure of material 2 sintered at 1410 °C.

TABLE IV Material properties of Y-TZP ceramics based on different raw materials

Property	Sample 2	Sample 3	Sample 4
Density (g/cm^3)	6.053	5.938	5.933
Bending strength (MPa)	1057	697	596
Standard deviation (MPa)	65	43	51
Weibull modulus	20	20	14
Fracture toughness (MPa$\sqrt{m}$)	9	7.3	6.6

bending strength is excellent in material 2. Also material 3 shows an acceptable strength value, especially taking into account the high Weibull modulus of 20. Material 2 has additionally a very high fracture toughness of 9 MPa$\sqrt{m}$.

4. Discussion

While in coprecipitated powders the tetragonal phase is already formed below the martensitic phase transformation temperature, in yttria-coated zirconia powders the tetragonal solid solution is formed at higher temperatures. It is clear that at the transformation temperature of 1175 °C the monoclinic → tetragonal phase transformation takes place. It is however surprising that it takes place very slowly. Even at 1300 °C the phase transformation is kinetically controlled. The transformation of pure zirconia (Fig. 1) is much faster and takes place very rapidly at 1175 °C, which corresponds to the expected martensitic phase transformation. Based on these results it is assumed that the formation of tetragonal solid solutions in the yttria-coated powder depends on the diffusion rate of yttria. As high temperature X-ray investigations have shown, the higher the temperature, the faster the tetragonal modification. This is a further aspect which relates to the thermodynamically and kinetically yttria diffusion-controlled phase transformation. It is assumed that during sintering diffusion-controlled phase transformation plays an important role in the densification behaviour.

Although the powders were prepared under the same conditions, the sintered materials showed very different compressibility and sintering behaviour. While in material 2 a density $\geqslant 6$ g/cm^3 can be realized very easily, such a density of parts having a very fine-grained and homogeneous microstructure was not achieved in materials 3 and 4. Regarding the mechanical strength and fracture toughness it has to be pointed out that material 2, which is based on a coated Y-TZP powder, shows excellent properties. In the materials based on coprecipitated powders which were prepared under the same conditions, the properties are worse. In material 4, which is based on the powder with the highest chemical purity, the mechanical strength is not acceptable. Material 4 is the material having the highest shrinkage during sintering, and the lowest density. Based on a theoretical density of 6.1 g/cm^3, a porosity of about 3% remains in the sintered material 4. This high porosity level explains the low strength of 600 MPa. Due to the relatively high Weibull modulus failures during the green body forming can be excluded. It seems more reasonable to assume that the pores remain during sintering because of a very high shrinkage rate, which is caused by the low green density, and high sinteractivity of the powder, which is caused by the high specific surface area.

Material 3 has about the same density as material 4. Although the specific surface area of powder 3 is lower than that of powder 4, the densification during the sintering process is assisted by glass forming oxides such as TiO_2, SiO_2, Al_2O_3 and CaO. It is assumed that a very thin amorphous grain boundary phase is responsible for the higher strength in material 3 compared to material 4. The Weibull modulus is 20. This value is extremely high for Y-TZP ceramics, because normally these materials show very high strengths but only marginal Weibull moduli, while PSZ ceramics normally have lower strengths and Weilbull moduli up to 25.

For materials 3 and 4 it seems reasonable that a pressure-supported densification process would lead to higher densities and strengths. This goal can be reached by a HIP-process, which can follow a presintering process at moderate temperatures in order to achieve a fine and homogeneous microstructure and to eliminate pores. At least for material 4 another approach is possible: optimization of the binder system in order to achieve a higher green density and a different shrinkage during sintering. This approach was shown to be successful in Y-TZP ceramics available on the market. Excellent strengths of about 1000 MPa are realized.

In material 2 densities of more than 99% are reached at moderate temperatures. The densification process is assisted by the specific surface area, grain size distribution, high green density and the behaviour of the monoclinic → tetragonal phase transformation, which still takes place during the shrinkage process and leads to a very controlled densification process. The strength of the material is excellent, especially taking into account the extremely low standard deviation; expressed by a Weibull modulus of 20.

Regarding the fracture toughness, again material 2 is excellent compared to materials 3 and 4. While in materials 3 and 4, based on coprecipitated Y-TZP powders, the distribution of yttria remains very homogeneous, in the coated powder there is a gradient within every grain from the surface to the centre [6]. In the centre of every grain there is virtually no stabilization, which is proved by chemical analysis in TEM investigations. By mechanically induced stresses the well-known phase transformation is more effective in material 2 than in the materials 3 and 4 and leads to the excellent fracture toughness [7, 8]. Furthermore it has to be pointed out that the amount of yttria needed for stabilization of the tetragonal phase is lower than in the coprecipitated raw materials. This is also related to the yttria gradient within the zirconia grains.

Due to the fact, that in Y-TZP ceramics the concentration of yttria at the surface of every grain is higher than in the centre of the grain, those materials are expected to have a higher resistivity to hydrothermal decomposition [9]. This assumption is related to microstructural studies on different Y-TZP ceramics. In these investigations it was demonstrated that the Y-TZP material having the most inhomogeneous distribution of yttria within the grains, shows the highest resistivity to hydrothermal attack.

5. Conclusions

- Y-TZP ceramics based on yttria-coated powders show a diffusion-controlled phase transformation from monoclinic to tetragonal
- For stabilization of the tetragonal phase in coated powders lower amounts of yttria are needed than in coprecipitated powders.
- Y-TZP ceramics made from yttria-coated powders show excellent mechanical properties: high strength and high fracture toughness.
- Y-TZP ceramics made from coated powders are expected to have good resistivity to hydrothermal decomposition due to the yttria gradient within the zirconia grains.
- Y-TZP ceramics based on yttria-coated zirconia powders are very favourable for use in biomedical applications as well as Y-TZP materials based on coprecipitated powders.

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